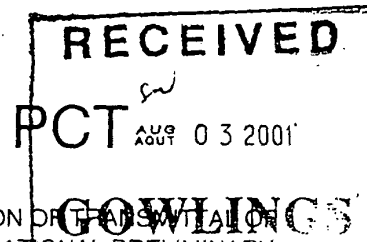


From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

SECHLEY, Konrad, A.  
Gowling Lafleur Henderson LLP  
Suite 2600  
160 Elgin Street  
Ottawa, Ontario K1P 1C3  
CANADA



NOTIFICATION OF TRANSMISSION  
OF THE INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT  
(PCT Rule 71.1)

Date of mailing  
(day/month/year) 26.07.2001

Applicant's or agent's file reference  
O8-878545WO1

**IMPORTANT NOTIFICATION**

International application No.  
PCT/CA00/00868

International filing date (day/month/year)  
28/07/2000

Priority date (day/month/year)  
29/07/1999

Applicant  
ENSYN GROUP, INC. et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.
4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/



European Patent Office  
D-80298 Munich  
Tel. +49 89 2399 - 0 Tx: 523656 epmu d  
Fax: +49 89 2399 - 4465

Authorized officer

Aperribay, I

Tel. +49 89 2399-8154





# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference <b>O8-878545WO1</b>	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416) <b>FOR FURTHER ACTION</b>	
International application No. <b>PCT/CA00/00868</b>	International filing date (day/month/year) <b>28/07/2000</b>	Priority date (day/month/year) <b>29/07/1999</b>
International Patent Classification (IPC) or national classification and IPC <b>C08L61/06</b>		
Applicant <b>ENSYN GROUP, INC. et al.</b>		
1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.  2. This REPORT consists of a total of 6 sheets, including this cover sheet.  <input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).  These annexes consist of a total of sheets.		
3. This report contains indications relating to the following items:  <div style="margin-left: 40px;">           I <input checked="" type="checkbox"/> Basis of the report            II <input checked="" type="checkbox"/> Priority            III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability            IV <input type="checkbox"/> Lack of unity of invention            V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement            VI <input type="checkbox"/> Certain documents cited            VII <input checked="" type="checkbox"/> Certain defects in the international application            VIII <input checked="" type="checkbox"/> Certain observations on the international application         </div>		
Date of submission of the demand  <b>22/02/2001</b>	Date of completion of this report  <b>26.07.2001</b>	
Name and mailing address of the international preliminary examining authority:  <div style="display: flex; align-items: center;"> <div>             European Patent Office              D-80298 Munich              Tel. +49 89 2399 - 0 Tx: 523656 epmu d              Fax: +49 89 2399 - 4465           </div> </div>	Authorized officer  <b>Hutton, D</b>  Telephone No. +49 89 2399 8660	





**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/CA00/00868

**I. Basis of the report**

1. With regard to the elements of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

**Description, pages:**

1-64 as originally filed

**Claims, No.:**

1-30 as originally filed

**Drawings, sheets:**

1/6-6/6 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/CA00/00868

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**II. Priority**

1. ☐ This report has been established as if no priority had been claimed due to the failure to furnish within the prescribed time limit the requested:

☐ copy of the earlier application whose priority has been claimed.

☐ translation of the earlier application whose priority has been claimed.

2. ☒ This report has been established as if no priority had been claimed due to the fact that the priority claim has been found invalid.

Thus for the purposes of this report, the international filing date indicated above is considered to be the relevant date.

3. Additional observations, if necessary:  
see separate sheet

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Yes:	Claims
	No:	Claims 1-13, 15-22, 25-30
Inventive step (IS)	Yes:	Claims
	No:	Claims 1-30
Industrial applicability (IA)	Yes:	Claims 1-30
	No:	Claims

2. Citations and explanations  
see separate sheet

**VII. Certain defects in the international application**

The following defects in the form or contents of the international application have been noted:  
see separate sheet





**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/CA00/00868

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**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:  
**see separate sheet**



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/CA00/00868

The following documents have been considered in formulating this report:-

- D1: CA-A-2228418
- D2: WO-A-9111499
- D3: WO-A-9101341
- D4: US-A-4942269

**Section II** :- Priority

Document D1 is a previous application from the same inventors filed on 30.01.1998 and published on 30.07.1999. This document discloses natural resin compositions, phenol/formaldehyde based adhesives based on such natural resins and a process for the production of such resins based on the fast pyrolysis of biomass falling within the scope of the present claims. The present application claims priority from US 09/364,610 filed on 29.07.1999. However the validity of this claimed priority date is called in to question in the light of D1. Thus it would appear that the priority claimed is invalid and the effective date for assessing priority defaults to the international filing date. Thus D1 becomes relevant in examining Novelty and Inventive Step. (See PCT Preliminary Examination Guidelines , Section IV, Chapter V, V-1,V-2).

**Section V**:- Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

**Novelty**:- Document D1 see Section II above. The disclosures of D1 would appear to fall within the scope of present claims 1-13,15-20-22, and 25-30.

As indicated at p.27, Example 1 of the present application , the natural resins of the present application were prepared using the fast pyrolysis process known from D2.

Since the subject-matter of the present process claims 21 and 22 is disclosed in D2, (see in particular pages 20-25) and the Examples , said claims are not novel.

Furthermore it would appear that since similar process conditions are employed the resin obtained in D2 will also fall within the scope of the present claims. D3 also describes a fast pyrolysis process for the production of natural resins (cf. p.4,I.3 et seq.) and their use in the preparation of phenolic resins and adhesives. In the absence of any clear distinguishing feature in the process claimed, these resins are also taken to fall within the scope of the present claims.

**Inventive Step**:- No comprehensive assessment of the presence of an Inventive Step is possible, however the treatment of fractions with water would (cf. D1 and D4) appear to represent a routine measure in the work up of such fractions and not in itself as involving the presence of an Inventive Step.



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/CA00/00868

**Section VII** :- Certain defects in the international application

To meet the requirements of Rule 5.1(a)(ii) PCT, the document D1 should be identified in the description and the relevant background art disclosed therein should be briefly discussed.

**Section VIII** :- Certain observations on the international application

- (i) The use of the word "about" in connection with the limits of ranges in the claims leads to uncertainty as to the exact scope of protection sought by these claims. This word should be excised from the claims and description where used in this context.
- (ii) The term "a pleasant smoky odour" used in claim 1 is vague and unclear and leaves the reader in doubt as to the exact meaning of the technical features to which it refers, thereby rendering the definition of the subject-matter of said claim unclear (Article 6 PCT).
- (iii) The term "natural resin" should be defined in the claims.
- (iv) Many of the technical features of the claims lack the requisite support in the description.
- (v) Claim 23 is unclear as the nature of the pretreatment step is not specified.



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## PATENT COOPERATION TREATY

PCT/CA00/00868

PCT

From the INTERNATIONAL BUREAU

To:

SECHLEY, Konrad, A.  
Gowling Lafleur Henderson LLP  
Suite 2600  
160 Elgin Street  
Ottawa, Ontario K1P 1C3  
CANADA

INFORMATION CONCERNING ELECTED  
OFFICES NOTIFIED OF THEIR ELECTION

(PCT Rule 61.3)

Date of mailing (day/month/year) 05 April 2001 (05.04.01)		
Applicant's or agent's file reference O8-878545WO1		
<b>IMPORTANT INFORMATION</b>		
International application No. PCT/CA00/00868	International filing date (day/month/year) 28 July 2000 (28.07.00)	Priority date (day/month/year) 29 July 1999 (29.07.99)
Applicant ENSYN GROUP, INC. et al		

1. The applicant is hereby informed that the International Bureau has, according to Article 31(7), notified each of the following Offices of its election:

AP : GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW

EP : AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE

National : AU, BG, CA, CN, CZ, DE, IL, JP, KP, KR, MN, NO, NZ, PL, RO, RU, SE, SK, US

2. The following Offices have waived the requirement for the notification of their election; the notification will be sent to them by the International Bureau only upon their request:

EA : AM, AZ, BY, KG, KZ, MD, RU, TJ, TM

OA : BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG

National : AE, AG, AL, AM, AT, AZ, BA, BB, BR, BY, BZ, CH, CR, CU, DK, DM, DZ, EE, ES, FI, GB,  
GD, GE, GH, GM, HR, HU, ID, IN, IS, KE, KG, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MW,  
MX, MZ, PT, SD, SG, SI, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW

3. The applicant is reminded that he must enter the "national phase" **before the expiration of 30 months from the priority date** before each of the Offices listed above. This must be done by paying the national fee(s) and furnishing, if prescribed, a translation of the international application (Article 39(1)(a)), as well as, where applicable, by furnishing a translation of any annexes of the international preliminary examination report (Article 36(3)(b) and Rule 74.1).

Some offices have fixed time limits expiring later than the above-mentioned time limit. For detailed information about the applicable time limits and the acts to be performed upon entry into the national phase before a particular Office, see Volume II of the PCT Applicant's Guide.

The entry into the European regional phase is postponed **until 31 months from the priority date** for all States designated for the purposes of obtaining a European patent.

<p>The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland</p> <p>Facsimile No. (41-22) 740.14.35</p>	<p>Authorized officer:</p> <p>Charlotte ENGER</p> <p>Telephone No. (41-22) 338.83.38</p>
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## PATENT COOPERATION TREATY

PCT



REC'D 30 JUL 2001

WIPO

PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference O8-878545WO1	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/CA00/00868	International filing date (day/month/year) 28/07/2000	Priority date (day/month/year) 29/07/1999
International Patent Classification (IPC) or national classification and IPC C08L61/06		
Applicant ENSYN GROUP, INC. et al.		
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 6 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of sheets.</p>		
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> <li>I <input checked="" type="checkbox"/> Basis of the report</li> <li>II <input checked="" type="checkbox"/> Priority</li> <li>III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</li> <li>IV <input type="checkbox"/> Lack of unity of invention</li> <li>V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</li> <li>VI <input type="checkbox"/> Certain documents cited</li> <li>VII <input checked="" type="checkbox"/> Certain defects in the international application</li> <li>VIII <input checked="" type="checkbox"/> Certain observations on the international application</li> </ul>		
Date of submission of the demand  22/02/2001	Date of completion of this report  26.07.2001	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer  Hutton, D  Telephone No. +49 89 2399 8660 	



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/CA00/00868

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

**Description, pages:**

1-64 as originally filed

**Claims, No.:**

1-30 as originally filed

**Drawings, sheets:**

1/6-6/6 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:



# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/CA00/00868

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

## II. Priority

1. ☐ This report has been established as if no priority had been claimed due to the failure to furnish within the prescribed time limit the requested:

☐ copy of the earlier application whose priority has been claimed.

☐ translation of the earlier application whose priority has been claimed.

2. ☒ This report has been established as if no priority had been claimed due to the fact that the priority claim has been found invalid.

Thus for the purposes of this report, the international filing date indicated above is considered to be the relevant date.

3. Additional observations, if necessary:  
**see separate sheet**

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims
	No:	Claims 1-13,15-22,25-30
Inventive step (IS)	Yes:	Claims
	No:	Claims 1-30
Industrial applicability (IA)	Yes:	Claims 1-30
	No:	Claims

2. Citations and explanations  
**see separate sheet**

## VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:  
**see separate sheet**



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/CA00/00868

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**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

**see separate sheet**





**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

---

International application No. PCT/CA00/00868

The following documents have been considered in formulating this report:-

D1: CA-A-2228418

D2: WO-A-9111499

D3: WO-A-9101341

D4: US-A-4942269

**Section II** :- Priority

Document D1 is a previous application from the same inventors filed on 30.01.1998 and published on 30.07.1999. This document discloses natural resin compositions, phenol/formaldehyde based adhesives based on such natural resins and a process for the production of such resins based on the fast pyrolysis of biomass falling within the scope of the present claims. The present application claims priority from US 09/364,610 filed on 29.07.1999. However the validity of this claimed priority date is called in to question in the light of D1. Thus it would appear that the priority claimed is invalid and the effective date for assessing priority defaults to the international filing date. Thus D1 becomes relevant in examining Novelty and Inventive Step. (See PCT Preliminary Examination Guidelines , Section IV, Chapter V, V-1,V-2).

**Section V**:- Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Novelty:- Document D1 see Section II above. The disclosures of D1 would appear to fall within the scope of present claims 1-13,15-20-22, and 25-30.

As indicated at p.27, Example 1 of the present application , the natural resins of the present application were prepared using the fast pyrolysis process known from D2. Since the subject-matter of the present process claims 21 and 22 is disclosed in D2, (see in particular pages 20-25) and the Examples , said claims are not novel.

Furthermore it would appear that since similar process conditions are employed the resin obtained in D2 will also fall within the scope of the present claims. D3 also describes a fast pyrolysis process for the production of natural resins (cf. p.4,I.3 et seq.) and their use in the preparation of phenolic resins and adhesives. In the absence of any clear distinguishing feature in the process claimed, these resins are also taken to fall within the scope of the present claims.

Inventive Step:- No comprehensive assessment of the presence of an Inventive Step is possible, however the treatment of fractions with water would (cf. D1 and D4) appear to represent a routine measure in the work up of such fractions and not in itself as involving the presence of an Inventive Step.



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

---

International application No. PCT/CA00/00868

**Section VII** :- Certain defects in the international application

To meet the requirements of Rule 5.1(a)(ii) PCT, the document D1 should be identified in the description and the relevant background art disclosed therein should be briefly discussed.

**Section VIII** :- Certain observations on the international application

- (i) The use of the word "about" in connection with the limits of ranges in the claims leads to uncertainty as to the exact scope of protection sought by these claims. This word should be excised from the claims and description where used in this context.
- (ii) The term "a pleasant smoky odour" used in claim 1 is vague and unclear and leaves the reader in doubt as to the exact meaning of the technical features to which it refers, thereby rendering the definition of the subject-matter of said claim unclear (Article 6 PCT).
- (iii) The term "natural resin" should be defined in the claims.
- (iv) Many of the technical features of the claims lack the requisite support in the description.
- (v) Claim 23 is unclear as the nature of the pretreatment step is not specified.

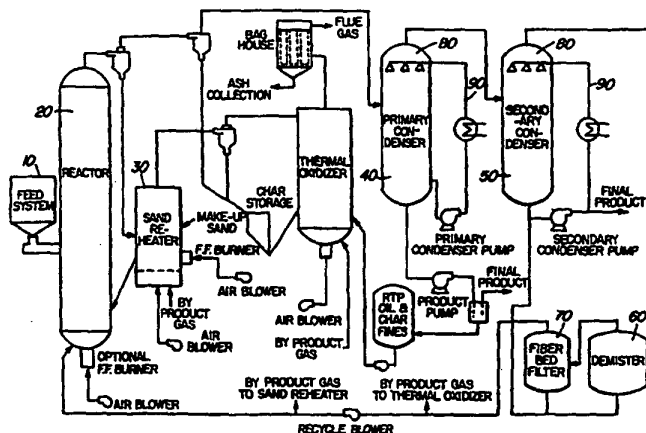




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>C10C 5/00, C08H 5/04, C08G 16/02, C08L 97/02</b>		A1	(11) International Publication Number: <b>WO 99/38935</b>
			(43) International Publication Date: <b>5 August 1999 (05.08.99)</b>
(21) International Application Number: <b>PCT/CA99/00051</b>		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: <b>29 January 1999 (29.01.99)</b>			
(30) Priority Data: <b>2,228,418                      30 January 1998 (30.01.98)      CA</b>			
(71) Applicant (for all designated States except US): <b>ENSYN TECHNOLOGIES INC. [CA/CA]; Suite 201, 380 Hunt Club Road, Ottawa, Ontario K1V 1C1 (CA).</b>			
(72) Inventors; and			
(75) Inventors/Applicants (for US only): <b>FREEL, Barry [CA/CA]; 6489 Greely West Drive, Greely, Ontario K4P 1E8 (CA). GRAHAM, Robert [CA/CA]; 6847 Hiram Drive, Greely, Ontario K4P 1A2 (CA).</b>		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(74) Agents: <b>SECHLEY, Konrad, A. et al.; Gowling, Strathy &amp; Henderson, Suite 2600, 160 Elgin Street, Ottawa, Ontario K1P 1C3 (CA).</b>			

(54) Title: NATURAL RESIN FORMULATIONS



## (57) Abstract

This invention is directed to a method of preparing a natural resin by liquefying wood, bark, forest residues, wood industry residues, or other biomass using fast pyrolysis in order to produce product vapours and char. Following removal of the char from the product vapours, a first set of compounds are removed from the product vapours by rapid quenching in order to obtain a remaining selected product vapour from which a natural resin is obtained. The natural resin comprises a total phenolic content from about 30 % to about 80 % (w/w), and is further characterized as having a pleasant smoky odour. The natural resin has surprisingly been found to be suitable for use within adhesive formulations without requiring any further extraction or fractionation procedures. Adhesives comprising up to 60 % natural resin have been prepared and tested in board production and found to exhibit similar properties associated with commercially available resins. The natural resin may substitute for phenol, or for both phenol and formaldehyde within phenol-containing resins. Similarly, the natural resin can replace a substantial part of the components within urea-containing resins.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
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AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
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# INTERNATIONAL SEARCH REPORT

Int. Application No  
PCT/CA 99/00051

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C10C5/00 C08H5/04 C08G16/02 C08L97/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C10C C08H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 1 598 547 A (EMILE AUGUSTIN BARBET) 31 August 1926 see page 1, line 23 - line 75 ---	1, 20, 23
A	US 4 233 465 A (GALLIVAN ET AL.) 11 November 1980 see claims ---	1, 5, 17
A	WO 91 01341 A (BIOCARBONS CORPORATION) 7 February 1991 ---	
A	WO 91 11499 A (ENSYN ENGINEERING ASSOCIATES INC.) 8 August 1991 cited in the application -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

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Date of the actual completion of the international search

10 June 1999

Date of mailing of the international search report

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Name and mailing address of the ISA

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int .tional Application No

PCT/CA 99/00051

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 1598547 A		NONE	
US 4233465 A	11-11-1980	NONE	
WO 9101341 A	07-02-1991	US 5034498 A CA 2062780 A,C JP 7033421 B JP 4504588 T US 5115084 A	23-07-1991 20-01-1991 12-04-1995 13-08-1992 19-05-1992
WO 9111499 A	08-08-1991	CA 2009021 A CS 9100223 A DE 69106347 D DE 69106347 T DK 513051 T EP 0513051 A ES 2065674 T FI 923434 A PL 168638 B US 5792340 A	31-07-1991 15-04-1992 09-02-1995 11-05-1995 18-04-1995 19-11-1992 16-02-1995 30-07-1992 29-03-1996 11-08-1998



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Our Case No. 6340/12

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE  
APPLICATION FOR UNITED STATES LETTERS PATENT

INVENTORS:	BARRY FREEL REGI GIROUX ROBERT GRAHAM
TITLE:	NATURAL RESIN FORMULATIONS
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## NATURAL RESIN FORMULATIONS

The present invention relates to the production and use of a natural resin, derived from wood, bark, forest residues, wood industry residues and other biomass materials using fast pyrolysis, and its use as an adhesive in the manufacture of manufactured wood products.

### BACKGROUND OF THE INVENTION

“Resin” is a generic term used to describe both natural and synthetic glues which derive their adhesive properties from their inherent ability to polymerize in a consistent and predictable fashion. The vast majority of modern industrial resins are synthetic, and are normally derived from petroleum feedstocks. Two of the most important classes of synthetic resins, in terms of production volume and total sales are phenol formaldehyde (P/F) and urea formaldehyde (U/F) resins. In both cases, the principal market application is for use as a glue binder in man-made wood products.

Phenol formaldehyde (P/F) resin, because of its resistance to moisture, has a particular value in external (outdoor) or damp environments. It is therefore, the leading adhesive used for the manufacture of plywood, oriented strand board (OSB) and wafer board (Sellers, 1996). P/F resins are also widely used in laminates, insulation, foundry materials, moulding compounds, abrasives and friction materials for the transportation industry (ie., clutch facings, disk facings and transmission components). As its name suggests, the principal ingredients in P/F adhesives are phenol and formaldehyde. However, the finished product is actually a mixture of P/F, caustic, and water. Assorted fillers, extenders and dispersion agents may then be added for specific adhesive applications.

The formaldehyde ingredient in P/F resin is derived from methanol, normally produced from natural gas. The phenol ingredient is typically manufactured from benzene and propylene via a cumene intermediate. In addition to P/F adhesive manufacture, phenol is used in the manufacture of other important products, for example, Bisphenol A and Caprolactam. Bisphenol A is a principal component in polycarbonates

used in automotive parts, compact discs and computer discs, and Caprolactam is a raw material for Nylon 6, used within stain resistant carpets.

When mixed together in water and with caustic added as a catalyst, phenol and  
5 formaldehyde undergo a condensation reaction to form either ortho- or para-  
methylophenol. The resultant PF resin, as shipped to market, is a dark brown liquid  
which is polymerized and cross-linked to an intermediate degree. It is then cured in the  
final board, laminate or other product without catalyst simply with the addition of heat  
at which time the final polymerization and cross-linking take place via condensation  
10 reactions. The release of free formaldehyde during the resin manufacture and resin use  
stages is a concern from a health and safety perspective. Furthermore, the costs  
associated with formaldehyde production have increased and there is a need in the art  
for alternative materials for use as wood adhesives and binders.

15 One alternative for phenol that has been considered is lignin. Lignin and P/F  
formaldehyde resins are structurally very similar. Lignin is a random network polymer  
with a variety of linkages, based on phenyl propane units. Lignin-based adhesive  
formulations have been tested for use within plywood, particle board and fibre board  
manufacture. The addition of polymeric lignin to P/F formulations has been found to  
20 prematurely gel the P/F resin thereby reducing shelf life, limiting permeation of the  
lignin-P/F resin into the wood and producing an inferior mechanical bond (Kelley  
1997).

Pyrolysis of lignin has been considered as a potential approach to upgrading  
25 lignin to more usable phenolic type resins. While relatively mild thermal or thermo-  
catalytic processing at low pressures can be used to break the lignin macromolecules  
into smaller macromolecules, lignin segments and monomeric chemicals, such  
procedures may cause condensation reactions producing highly condensed structures  
such as char and tar, rather than depolymerized lignin fragments or monomeric  
30 chemicals.

A further alternative for the production of phenolic compounds involves use of pyrolytic oils produced in the fast pyrolysis of wood and other biomass. These pyrolytic oils are comprised of a complex mixture of compounds including phenol, guaiacol, syringol and para substituted derivatives, carbohydrate fragments, polyols, organic acids, formaldehyde, acetaldehyde, furfuraldehyde and other oligomeric products (Pakdel et al 1996). However, wood-derived lignin and lignin-rich pyrolytic bio-oils have lacked consistency and have exhibited inferior properties when compared with phenol-formaldehyde resins (Chum et al. 1989; Scott 1988; Himmelblau 1997; Kelley et al., 1997).

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Due to the complexity of pyrolytically-derived bio-oils, further processing is required in order to obtain suitable fractions useable as a replacement for phenol, or to be considered as an extender for petroleum-derived phenol within P/F resin formulations. Typically the phenolic derived from pyrolysis oils requires separation prior to use in order to remove impurities. One such method involves water extraction of the whole-oil, followed by precipitation and centrifugation or filtration and drying of the non-aqueous fraction to prepare a "pyrolytic lignin" fraction (Scott 1988). However, adhesive formulations prepared using pyrolytic lignin were found to be inferior to P/F resin formulations in both colour and odour, and required long press times in order to avoid de-lamination of waferboards. Tests indicated that none of the pyrolytic lignin samples meet the internal bond (IB) test requirement (Scott 1988, see pp. 91-92) .

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In US 4,209,647 (June 24, 1980) a fractionation method for the preparation of a phenol- enriched pyrolytic oil is disclosed which involved a multistep process that selectively solubilized neutral phenols, and organic acids of the whole-oil with NaOH followed by extraction with methylene chloride. However, this multistep process is costly, labourious, time consuming and involves the use of volatile solvents that are known to be health threatening.

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Another fractionation method involves adding ethyl acetate to whole-oil to produce ethyl acetate soluble and insoluble fractions, followed by a water wash and NaHCO<sub>3</sub> extraction of the ethyl acetate soluble fraction, with evaporation of the ethyl acetate to produce a fraction containing phenolic and neutrals (P/N) derived from the pyrolytic oil (Chum et al. 1989, US Patents 4,942,269, July 17, 1990, and 5,235,021, August 10, 1993). Preliminary results with the P/N fractions revealed that fractionated pyrolytic oils could be used within P/F resin compositions, as P/N containing resins exhibited equivalent gel times as noted for P/F resins. However, the fractionation protocol is not suitable for industrial scale production, nor is this process cost effective for the preparation of alternative components for use within P/F resins at a commercial scale (Kelley et al., 1997).

All of the process disclosed within the prior art as outlined above involve the extraction of a phenol-enhanced fraction from the whole pyrolytic oil product using solvents and alkali. None of the prior art discloses a method which is directed at producing a fraction of bio-oil suitable for adhesive use, yet that does not require any solvent extraction.

## **20 SUMMARY OF THE INVENTION**

The present invention relates to the production and use of a natural resin, derived from wood, bark and other biomass residues using fast pyrolysis. Specifically, the natural resins (NR) of this invention are obtained from the fast pyrolysis of wood products. The NR comprises a thermal fraction of the liquid product produced from fast pyrolysis of bio-mass

By the processes of the present invention, there is no need to extract a phenol enhanced portion using solvents and alkali. Rather the NR of this invention is selected as a thermal fraction from the whole bio-oil produced during the pyrolytic process.

The natural resins of the present invention can be directly used as a substitute for some of the phenol in phenol/formaldehyde, phenol urea formaldehyde, and phenol melamine urea formaldehyde resins used as adhesives in the manufacture of wood products or it can be used as a substitute of some of the phenol and some the formaldehyde components of phenol-containing formaldehyde resins. Furthermore, the NR of this invention can be used as a substitute within urea formaldehyde resins, and melamine urea formaldehyde, and related resins. With further processing to remove organic acids, a natural resin can be produced which can be used as a substitute for either some of the phenol component of a phenol-containing formaldehyde resin or for both the phenol and formaldehyde components of the resin, or as a substitute within urea formaldehyde type resins..

The natural resins of the present invention exhibit high reactivity due to the presence of a high number of active sites for binding and cross linking during polymerization.

According to the present invention there is provided a method of preparing a natural resin comprising:

- i) liquefying a suitable biomass using fast pyrolysis in order to produce product vapours and char;
- ii) removing the char from the product vapours;
- iii) removing a first set of components from the product vapours by rapid quenching thereby producing a remaining selected product vapour;
- iv) obtaining the natural resin from the remaining selected product vapour.

This invention also pertains to the above method wherein the first set of components is removed from the product vapours within a first condenser. Furthermore, this invention is directed to the method as defined above wherein, the natural resin is obtained from the selected product vapour using direct-liquid contact condensers, within a secondary condenser, and other down stream components including a demister and a filter bed.

This invention is also directed to a natural resin (NR) characterized by comprising a free phenol content from about 0.001% to about 0.1% (w/w), a total phenolic content from about 30% to about 80% (w/w), a pleasant smoky odour, and a pH greater than 2.0.

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Furthermore, this invention relates an NR as defined above further characterized by comprising a water content from about 10 to about 20 wt%, a density from about 1.0 to about 1.3 g/ml, a solids content from about 0.5 to about 1.0 wt%, an ash content from about 0.05 to about 0.5 (wt%), and a viscosity at 75°C greater than 70 (cSt). The NR as defined may also further be characterized by comprising a net caloric value of about 4355 cal/g (18.22 MJ/kg), and a gross caloric value of about 4690 cal/g (19.62 MJ/kg).

15 This invention is also directed to an adhesive composition that comprises the NR as defined above. Furthermore, this invention is directed to an adhesive composition comprising NR from about 1% to about 40% (w/w) of the adhesive composition.

20 This invention is also directed to an adhesive composition as defined above comprising a second adhesive resin selected from a phenol-containing or urea containing formaldehyde resin. Furthermore, this invention relates to an adhesive composition as defined above wherein the phenol-containing or urea-containing formaldehyde resin is selected from the group consisting of phenol formaldehyde, urea formaldehyde, phenol melamine urea formaldehyde, melamine urea formaldehyde, and phenol urea formaldehyde.

25 This invention also relates to an adhesive composition as defined above wherein the NR comprises from about 20 to about 40% (w/w) of the adhesive composition. Furthermore, the adhesive composition of this invention may further be characterized in that a portion of the formaldehyde, within the formaldehyde-phenol resin is replaced with NR, and wherein the NR replaces up to about 50% of the formaldehyde content

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of the resin. Preferably the adhesive composition comprises a formaldehyde:phenol ratio from about 1.5:1 to about 3:1. This invention is also directed to an adhesive composition wherein a portion of the formaldehyde within a urea-formaldehyde resin is replaced with NR.

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This invention also relates to a natural resin that is washed, and to mixtures of natural resin, comprising the natural resin define above and washed natural resin. Furthermore, this invention is directed to adhesive compositions comprising washed natural resin and natural resin mixtures. This invention also includes phenol-  
10 containing formaldehyde resins comprising washed natural resin that replaces up to 100% of the phenol content of the phenol-containing resin.

This invention also embraces a wood product prepared using the adhesive compositions as defined above. Preferably, the wood product is selected from the  
15 group consisting of laminated wood, plywood, particle board, high density particle board, oriented strand board, medium density fiber board, hardboard or wafer board. Furthermore, the wood product prepared using the adhesive composition of this invention is used for exterior applications.

20 Use of a fast pyrolysis process to produce the bio-oil is beneficial in that the fast pyrolysis process depolymerizes and homogenizes the natural glue component of wood, that being lignin, while at the same time other constituents are also depolymerized including cellulose and hemicellulose. The yield of NR, depending upon the biomass feedstock varies from 15-20% of the feedstock and exhibits  
25 properties that are useful within, for example, phenol-containing, or urea-containing formaldehyde resin compositions. The natural resin so produced can be substituted for some of the phenol, or some of the phenol and formaldehyde, content within phenol-containing formaldehyde resins, and such formulations meet or exceed current phenol formaldehyde resin industry specifications. Furthermore, NR can substitute for some  
30 of the formaldehyde within urea-containing formaldehyde resins. With removal of the

organic acids, the NR can completely substitute for the phenol content in phenol resins, and can also be used within urea-containing formaldehyde resin formulations.

## 5     **BRIEF DESCRIPTION OF THE DRAWINGS**

These and other features of the invention will become more apparent from the following description in which reference is made to the appended drawings wherein:

0     **FIGURE 1** shows a schematic of a fast pyrolysis system.

**FIGURE 2** shows the relationship between the viscosity of NR with increased temperature.

5     **FIGURE 3** shows the infrared spectra obtained from, **FIGURE 3A**: NR, and **FIGURE 3B**: alkali NR. The bands of the spectra are assigned as follows:

1. O-H stretchings of carboxylic acids, alcohols and phenols (this band is not selective);
2. C-H stretchings of aromatic and aliphatic compounds;
- 10     3. C=O stretchings of carboxylic acids and aldehydes/ketones;
4. 4'. aromatic rings, in-plane skeletal bandings;
5. O-H phenolic banding;
6. C-O stretching of primary alcoholic groups.

## 15     **DESCRIPTION OF PREFERRED EMBODIMENT**

The present invention relates to the production and use of a natural resin, derived from wood bark and other biomass residues using fast pyrolysis.

30     By "bio-oil" or "whole-oil" it is meant the whole liquid fraction obtained following the fast pyrolysis of wood or other biomass. The whole oil is obtained from

the product vapour which is produced along with char following pyrolysis. Upon removal of the char the product vapour is condensed and collected within one or more condensers which are typically linked in series. Whole-oil, or bio-oil refers to the combination of the condensed products obtained from all of the condensers.

5

By "phenolics" it is meant polymeric phenols derived from lignin (lignin is a phenolic polymer which holds wood and bark fibres together and which gives wood its strength).

10 By "enhancers" it is meant carbonyl compounds, typically light aldehydes and ketones.

By "selected product vapour" it is meant the product vapour that remains a vapour following removal of char and the subsequent removal of other pyrolytic products condensed by at least one rapid quenching step. The selected product vapour is typically characterized in having a lower acid content than a product obtained as a result of the earlier, at least one quenching step. Furthermore, the selected product vapour comprises a higher molecular weight, viscosity, pH, phenolics content when compared with the earlier obtained product.

20 By "phenol-containing formaldehyde resin" it is meant adhesive compositions that comprises phenol as one of its ingredients. Such resins include but are not limited to phenol formaldehyde (PF), phenolic melamine urea formaldehyde (PMUF), and phenol urea formaldehyde (PUF) resins. Similarly, by "urea-containing formaldehyde resins" it is meant adhesive compositions comprising urea as one of its ingredients, for example, but not limited to, urea formaldehyde (UF), phenol urea formaldehyde (PUF), phenol melamine urea formaldehyde (PMUF), and melamine urea formaldehyde (MUF) resins. Without wishing to be bound by theory, it is thought that the addition of NR to urea-containing resins adds or complements the phenol content of these resins due to the high phenolic content of NR. Therefore, a UF resin that is partially replaced with NR may be considered a PUF-like resin.

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The natural resin (NR) of this invention is not a whole bio-oil product, rather it is a selected refined fraction of the whole liquid product, preferably produced from the fast pyrolysis of wood. However, other processes that are able to liquefy wood may also be used to prepare a product from which a NR may be obtained. The refined  
5 fraction is primarily comprised of depolymerised lignin and other reactive components including phenolics which provide an array of active sites for binding and cross linking within NR formulations. Non-reactive components are removed during the preparation of the NR. The isolated NR fraction is not subject to solvent or other fractionation processes used in the prior art, nor is it condensed (i.e. subject to condensation  
10 reactions) as would be typically done for conventional, or vacuum pyrolysis liquid products. Without wishing to be bound by theory, it is possible that the omission of such condensation reactions during the production of the NR of this invention is a primary reason for the high reactivity of NR as a resin agent.

15 Fast pyrolysis of wood or other biomass residues results in the preparation of product vapours and char. After removal of the char components from the product stream, the product vapours are condensed to obtain a whole-oil, or bio-oil product from pyrolysis. A suitable fast pyrolysis process for preparing such a bio-oil is described in WO 91/11499 (Freel and Graham, published August 8, 1991), and is  
20 diagrammatically presented in Figure 1. Briefly, the system includes a feed system (10), a reactor (20), a particulate inorganic heat carrier reheating system (30), and for the purposes of the invention described herein, primary (40) and secondary (50) condensers, through which the product vapours produced during pyrolysis are cooled and collected using a suitable condenser means (80). The NR of this invention is a  
25 product obtained from the secondary condenser, de-mister (60) and fiber filter bed (70), or a combination thereof. However, it is to be understood that analogous fast pyrolysis systems, comprising different number or size of condensers, or different condensing means may be used for the selective preparation of the NR of this invention.

A portion of the product vapours produced during fast pyrolysis are rapidly quenched within the primary condensation collection means outlined above. This rapid quenching enables the selective separation of a selected product vapour from the condensed liquid product which remains within the primary condenser. NR is collected  
5 from the selected product vapour, obtained from components down stream from the primary condenser, for example, but not limited to, the secondary condenser, demister, and fiber filter bed. It is to be understood that other fast pyrolysis systems, with various condenser means arrangements may be effectively used to partially purify the product vapour by removing a liquid fraction from the product vapour and producing  
10 a selected product vapour, from which a NR fraction, analogous to the NR of this invention, maybe obtained.

The condenser system used within the fast pyrolysis reactor system, outlined in Figure 1, involves the use of direct-liquid contact condensers (80) to cool the  
15 pyrolytic oil product. In the preferred embodiment liquid, used within these condensers to cool the pyrolytic product, is obtained from the corresponding cooled primary or secondary condenser product (90; (Figure 1). However, as would be evident to one of skill in the art, any other compatible liquid for cooling the product within the secondary condenser may also be used for this purpose. Furthermore, it is  
20 considered within the scope of this invention that other scrubber or cooling means including heat exchanges comprising solid surfaces and the like may also be used for cooling the product vapours, including the selected product vapour.

By thermal fraction it is meant the process of obtaining a selective fraction of  
25 the product vapour obtained from fast pyrolysis following removal of products from the product vapour stream that are rapidly quenched (e.g. from about 500°C to about 20°C within milliseconds). Surprisingly, the product that is left as a selected product vapour following the rapid quenching step can be directly utilized as a replacement of constituents within adhesive resins, such as phenol formaldehyde, urea formaldehyde,  
30 or related resins as defined above.

Without wishing to be bound by theory, it is thought that the rapid quenching of product vapours within the first condenser removes compounds that interfere with the use of bio-oils within adhesive resin formulations. The products removed from the product vapour within the first condenser are those that are readily soluble and rapidly quenched. The less soluble compounds and those that form aerosols or some other form that assists in their remaining within the product vapour, are transferred to the secondary condenser. This transferred product vapour is then a selected product vapour, which is comprised of a predominantly phenolic fraction, and also containing aldehydes, and provides the NR with its desirable properties for use within adhesive formulations.

The NR of this invention may also be further processed to removed the organic acid content of the resin. Any suitable method may be employed for this process, for example, and not wishing to be limited to this method, the NR of this invention may be washed in water by mixing the NR in water, allowing phase separation to take place, and recovering the oil fraction. Such a processed NR is, for the purposes of this invention referred to as "NRP". The NRP, prepared in this manner, comprises the phenolic and aldehyde content of NR, with a dramatically reduced organic acid content when compared with NR, and is a more concentrate form of NR. As a result NRP contains up to about 80% (w/w) phenolics.

It has also been observed that NRP diluted with NR produces a product suitable for use within adhesive resin formulations. For example NR50 refers to a 50-50 mix of NRP and NR, however, as would be evident to one of skill in the art, other mixture ratios may also be obtained and used for the purposes disclosed herein.

The NR, or NRP so produced has been substituted for some of the phenol content within PF resins, and such formulations meet or exceed current PF resin industry specifications. More specifically NR has been substituted up to about 60% of the phenol content within PF resins, and NRP to about 100% of the phenol content within a PF resin. Resins so produced may comprise up to about 40% (w/w) of NR.

Similarly, NR has also been used as replacement within PMUF and, PUF resins. Furthermore, the NR of this invention has successfully replaced up to about 60% (w/w) of the urea formaldehyde within UF resins, and has been effectively used within PMUF and MUF resins.

5

As a result of selecting a specific thermal fraction for the preparation of NR, the recovery technique is more selective than solvent extraction-based methods. For example, the P/N fraction extracted using ethyl acetate (e.g. US 4,942,269; US 5,235,021), results in a fraction comprising any compound that is soluble in this solvent and that is co-extracted along with the desired-for resin compounds. Several of these co-extracted compounds are odorous (e.g. lactone, an acrid compound) while others dilute the P/N resin. The thermal recovery technique of this invention is selective in that essentially all of the desirable resin components (natural phenolics derived from lignin) are recovered, while other non-desired compounds are removed within other fractions. As a result, the NR of this invention exhibits many beneficial properties over prior art pyrolytic oil extractions and requires significantly less preparation. For example:

1. NR and NRP have a pleasant "smoky" odour, and lack the acrid smell of solvent extracted fractions - when used within adhesive applications, there is no residual odour. solvent extracted preparations, such as P/N extractions, requires further processing to remove the acrid smell;
2. the fractionation of other pyrolytic oils, including P/N recovery, requires add-on solvent extraction processes following the primary fast pyrolysis process, while the isolation of NR is a thermal fraction obtained during the primary fast pyrolysis process, and no further processing is required. Furthermore, there is no extra "add-on" equipment required for preparation of NR. The selected NR may be modified by fine tuning of the fast pyrolysis process conditions. If desired, the NR may be further processed (washed, extracted etc.) in

order to optimize properties of the NR as required within different applications;

- 5           3. in solvent extracted processes, including the process used to obtain P/N, the solvent reacts with residuals in the fraction that is not used for P/N, to form salts. These salts must be recovered using a recovery boiler requiring additional costs, and the residual bio-oil is not available for other commercial applications. The NR, on the other hand, is isolated as a thermal cut which still permits the remaining bio-oil to be  
10           processed as required for other commercial applications without contamination;
4. the fast pyrolysis method used for the preparation of bio-oil, including NR, has been successfully scaled up from bench-top trials to  
15           industrial/commercial production levels (see WO91/11499). Therefore, NR preparations are easily produced on a commercial scale.

#### **Characteristics of NR**

20           The NR produced by the method of this invention has been found to be consistent between batch to batch productions runs of NR (as tested when used for OSB production, see below), even when using different feedstocks including hardwood and softwood.

25           Molecular weight is typically used as an index for adhesive resin reactivity and viscosity, with higher molecular weights indicating higher viscosity, and a corresponding lack of active sites necessary for cross-linking and binding strength in commercial resin formulations. However, with the NR product prepared following the method of this invention, the relationship between molecular weight, viscosity and  
30           reactivity is not valid.



The free phenol content of a resin formulations is also used to determine the suitability of alternative materials in PF resin formulations. The NR produced following the method of this invention is characterised in having a very low free phenol content, from about 0.001 to about 0.05 % (w/w), yet the total phenolic content is quite high, from about 30% to about 50% (w/w) within NR, and up to about 80% with NRP. It is the phenolic content which is very reactive and provides an array of active sites for binding and cross linking within NR formulations.

Furthermore, the NR is characterized by the following parameters, however these parameters even though typical are obtained from one sample and variations in these values are to be expected:

	Water content (wt%)	pH	Density (g/ml)	Solid content (wt%)	Ash content (wt%)	Viscosity at 75°C (cSt)
NR	14	2.2	1.268	0.706	0.105	59.8

The viscosity of NR over a range of temperatures is presented in Figure 2.

The infrared spectra of NR and alkali NR are presented in Figure 3A and 3B, respectively. Similar spectra are observed for both NR samples. The 1700 cm<sup>-1</sup> band that corresponds to the carbonylic group (band identified as 3) is reduced in Figure 3B, since R-COOH becomes R-COO<sup>-</sup> under the alkali conditions.

The NR of this invention comprises from 10 to 20% water, however, NR is insoluble in water due to its low polarity and high content of non-polar organics. By increasing the pH of the NR (to about 10) and converting it into its phenoxide ion form it obtains a gum-like consistency, is water soluble and can be used within formaldehyde-phenol formulations. The NR is soluble in organic solvents for example acetone, methanol, ethanol and isopropanol. Due to the hydrophobicity of NR, it is chemically compatible in the formulation of phenolic-based resins. NR is soluble in

a mixture of water/phenol, and when reacted with formaldehyde, gives methanol-water soluble derivatives.

Infrared analysis of NR, and alkali NR are exhibited in Figure 2A and Figure 2B. The same bands are detected between the two NR samples, however, in the alkali NR (Figure 3B), the  $1700\text{ cm}^{-1}$  band (relating to the carbonylic group #3;  $\text{R-COOH}$ ) becomes  $\text{R-COO}^-$  under the alkali conditions.

Calometric analysis indicates that NR has a net caloric value of  $4355\text{ cal/g}$  ( $18.22\text{ MJ/kg}$ ), with a gross caloric value of  $4690\text{ cal/g}$  ( $19.62\text{ MJ/kg}$ ).

NR is stable and homogenous and has been stored in excess of 12 months without loss of its properties.

NRP preparations exhibit similar properties to those of NR with the notable exception that the phenolics content of NRP increases up to about 80% (w/w), and the pH is more neutral. The exact pH of NRP is difficult to determine as water is required for this test, however, the acid content of NRP can be determined using gas chromatography (GC). GC analysis indicate that up to 90% or more of the organic acid content of NR is removed as a result of the washing procedure. Due to the removal of the organic acid content, NRP is a more concentrated form of NR. The content of phenolics, and the pH of NR-NRP mixtures, e.g. NR50, will vary depending upon the proportions of NR or NRP within the mixture.

NR-50 is approximately 50% NRP and 50% raw NR. NR-50 is prepared by blending two NR products, raw NR from the process and NRP.

#### NR60

NR-60 is a liquid which is approximately 60% NRP. However, the term "NR60" is not representative of a single NR product. NR60 is not prepared by blending raw NR

and NRP as the case with NR-50. NR-60 is prepared from raw NR, after raw NR is devolatilised thereby concentrating the raw NR to NR-60 (i.e., increasing the NRP concentration by driving off non-NRP volatiles). The non-NRP volatiles may be driven off using any suitable means, for example, but not limited to, heat, or evaporation under vacuum. It is to be understood that the term "NR60" represents an NR that can comprise a variety of NRP concentrations depending upon the NRP content initially used. "NR60" therefore includes an NR that comprises from about 40% to about 90% NRP. NR60 may be obtained from a variety of lignocellulosic feedstock sources including softwood, hardwood, bark, white wood, or other lignocellulosic biomass feedstocks, for example, bagasse (sugar cane residue). The use of PF/NR60 resins are discussed in Examples 7-10, a specific NR60 resin formulation, obtained from bark, (NRB) is discussed in Example 10.

Unlike NR or NR-50, the characteristic smoky odour is significantly reduced in NR-60 during the devolatilisation/concentration process

NR-60 can be derived from NR or from selected NR fractions derived from the fast pyrolysis of wood as described above (ie. from certain condensers, filters, demisters, etc.), or from the whole raw bio-oil as produced in the pyrolysis process. NR fractions and whole bio-oil can be processed and concentrated in several ways in order to produce NR-60; evaporation or distillation (for example, falling film, vacuum distillation, wet film evaporation, etc., or selective condensation of the raw NR, NR fractions or whole bio-oil), selective precipitation, or any other physical or chemical process which removes, evaporates, isolates or otherwise drives off certain acids, volatiles, water and other light components which are less effective in terms of resin properties and which contain odorous components.

Without intending to limit the present invention in any manner, NR-60 can be prepared by heating NR material (ie., raw NR, NR fractions or whole bio-oil) under vacuum to a temperature which is sufficient to devolatilize odorous and non-resin components. The water content is monitored to determine the degree of devolatilization

so that a final water content of between about 1 and about 10% is obtained. Preferably the final water content is between about 3 and about 5%.

Once the desired degree of devolatilization has been reached, water is added back in order to reduce the NR-60 product viscosity to the desired spec. Typically, sufficient water is added to bring the water content to a level in the range of from about 10 to about 25%. Preferably the final water content is about 15 to about 18%.

Viscosity, acid content and NRP content determination for NR-60 comprising 60% NRP is characterized with acids (dry wt%) 2-4%; water content between 15-18%; NRP is about 60%, and viscosity at 70°C is in the range of 30 to 150cSt. An NR60 comprising a variety of NRP concentrations can be prepared in a similar fashion to that as indicated above.

A comparison of some of the characteristics of NR, NR50 and NRP are provided below:

Component	NR	NR50	NRP	NR60*
Acids (dry wt%)	10-12	5-10	0-5	2-4
Phenolics (dry wt%)	35-38	38-53	64-73	50-65
Enhancers (dry wt%)	12-15	15-19	22-27	-
pH	2.4-2.6	2.5-2.8	3+	~2.5
viscosity (70°C)cSt	81-115	100-300	300+	30-150
Water (wet wt%)	11-18	<18	<18	15-18%
average MW (Daltons)	500-1000	700-1200	1000-2000	-

\*These values may differ in NR60 depending upon the final concentration of NRP used in the NR60 formulation.

## NR-containing Phenol Formaldehyde (PF), or Urea Formaldehyde (UF) Resins

In order to formulate NR within phenol-containing formaldehyde, or urea-containing formaldehyde resins, phenol or urea, water, paraformaldehyde, and other ingredients of the adhesive are mixed together and heated if required to dissolve the ingredients. If heated, the mixture is cooled prior to the addition of NR. Caustic (for example NaOH) is added to the mixture containing phenol or urea, formaldehyde and NR, to a desired pH. The addition of caustic ensures the solubilization of the NR, and initiates the reaction. This mixture may then be heated or cooled, and more caustic added during the preparation of the resin, as required. The resin is typically maintained at 10°C until use, and exhibits similar stability associated with commercial PF resin formulations. Phenolic melamine urea formaldehyde (PMUF), melamine urea formaldehyde (MUF), phenol urea formaldehyde (PUF) resins are prepared in a similar manner.

15

NR can be added up to about 60% (w/w) of the phenol content of the resin, or in the case of NRP, up to about 100% (w/w) of the phenol content may be substituted by NRP. Furthermore, the formaldehyde content of phenol-containing or urea-containing resins may be substituted with NR due to the natural aldehydes present within NR, for example NR can be used to replace up to about 50% (w/w) of the formaldehyde content of these resins. Similarly, up to about 60% (w/w) of the urea-formaldehyde content of a UF resin may be replaced using NR. Therefore, PF, UF and related resins may be formulated that contain up to about 40% (w/w) NR of the total resin composition.

20

## Board manufacture using NR-containing adhesives

The phenol-containing or urea-containing formaldehyde resins prepared above may be used for the production of a range of board products, for example, but not limited to, laminate wood boards, plywood, particle board, high density particle board, oriented strand board, medium density fiber board, hardboard, or wafer board.

30

Preferably, NR-containing PF resins are used within boards to be subject to exterior use due to the excellent water repellency of the resin. Typically UF resins are not desired for outside use, however, NR-containing UF resins may have application for exterior use due to the reduced swelling observed in boards prepared with urea  
5 formaldehyde adhesives comprising NR, compared with boards prepared using commercial UF resin.

NR containing PF or UF resins can be used for the production of oriented strand board (OSB) as outlined below. However, it is to be understood that this  
10 application of NR-containing resin is not to be considered limiting in any manner, as other wood derived products prepared using commercially available PF, UF, or related resins, which are commonly known within the art, may be prepared using resin formulations comprising NR.

15 Oriented strand boards may prepared using standards methods that are known to those of skill in the art. For example, but not to be considered limiting in any manner, the production of OSB may involve the following parameters:

20 wood matrix:	particulate wood product, wood chips, wafers, veneer or plywood etc.
Panel thickness:	from about 1/16" to 2"
Resin content:	from about 0.5 to about 20.0%
Wax content:	from about 0.5 to about 5%
Mat moisture:	from about 2 to about 10%
25 Press time:	from about 2 min to 30 min
Press temperature:	from about 150 °C to about 275°C

It is to be understood that these parameters may be adjusted as required in order to produce a suitable board product using NR-containing resins of this invention.

Oriented strand boards, or other board types, as listed above, that are prepared using NR-containing PF resins are readily tested for suitability within the industry. For example, the OSB boards prepared above have been tested according to the Canadian product standard for OSB (CSA 0437.1-93, April 1993). These tests include; determination of density, internal bond (IB), modulus of rupture (MOR), and modulus of elasticity (MOE). Results of these tests indicate that phenol may be replaced by NR up to about 60% (or up to 100% in the case of NRP), and that urea-containing resins may also be replaced by up to 60% NR, and produce a OSB product that meets industrial standards, and that is equivalent to OSBs prepared using commercially available phenol-containing, or urea-containing formaldehyde resins. Furthermore, OSB boards prepared with NR-containing resins require less formaldehyde within resin formulations for equivalent cross-linking and binding properties as typically found with control resin formulations. Without wishing to be bound by theory, it is thought that the natural carbonyl components (such as aldehydes and ketones) within NR permits the use of less formaldehyde. In applications which require lower strength adhesive, the NR can be used alone without any addition of formaldehyde, but it is preferable to add formaldehyde to obtain a better resin. These carbonyl compounds have a molecular weight from about 30 to about 800 Daltons, and comprise about 23% of the NR.

20

The NR produced following the method of this invention has a dark brown colour, and when formulated into a resin, results in a dark reddish brown colour. However, during production runs using NR, OSB boards are lighter in colour than PF control boards. Furthermore, the NR has a mild, pleasant odour, yet OSB boards prepared using NR have no resultant odour. The odour can be reduced following heating of the NR, or through the removal of volatiles via flushing. The NR of this invention is also characterized by being acidic (pH ~2.3), however, the NR may be further processed, if desired to raise the pH, for example by washing NR in the presence of water, and recovering an NRP fraction which exhibits a higher content of phenolics, a more neutral pH, and is a more concentrate form of NR.

30

## Examples

### Example 1: Method for obtaining, and the characteristics of, NR

5           Natural resin was obtained using red maple feedstock within a fast pyrolysis reactor as described in WO 91/11499. Red maple feedstock is supplied to the reactor at a feedstock to heat carrier ratio of from about 5:1 to about 200:1. The char is rapidly separated from the product vapour/gas stream, and the product vapour rapidly quenched within the primary condenser using a direct liquid contact condenser. The  
10       compounds remaining within the product vapour are transferred to a secondary condenser linked to the primary condenser in series. The product vapour is then quenched using a direct-liquid contact condenser within the secondary condenser, and the condensed product collected. Any remaining product within the product vapour is collected within the demister and filter bed (see Figure 1). The secondary condenser  
15       product, demister and filter bed products are pooled together to comprise NR. The yield of NR, using red maple as a feedstock, is 18%.

          The NR is characterized as exhibiting a low free phenol content ranging from 0.001 to 0.1% (w/w); total phenolic content from about 35-80% (w/w); a dark brown colour  
20       and a mild, pleasant smoky odour; a pH of about 2.0 to about 3.9; insolubility in water; and solubility in organic solvents including acetone, methanol, ethanol and isopropanol.

          NR is readily washed with water to produce NRP which is characterized in  
25       having a more neutral pH, and up to 90% less organic acid content when compared with NR. Furthermore, the phenolic content of NRP is up to about 80% (w/w) or more, due to the removal of the organic acid component, and is a more concentrate form of NR.



A comparison of the products collected from the primary condenser (1°), NR (obtained from the secondary condenser, demister, and fiber filter bed) are presented below. The values for NRP and NR50 are presented for comparison:

Component	1°	NR	NR50	NRP
Acids (dry wt%)	15-20	10-12	5-10	0-5
Phenolics (dry wt%)	18-21	35-38	38-53	64-73
Enhancers (dry wt%)	6-8	12-15	15-19	22-27
pH	2.2-2.3	2.4-2.6	2.5-2.8	3+
viscosity (70°C) cSt	5-15	81-115	100-300	300+
Water (wet wt%)	18-26	11-18	<18	<18
average MW	100-300	500-1000	700-1200	1000-2000

#### Example 2: Replacement of phenol within NR-containing PF resins

The NR produced according to the method of Example 1 was formulated into a resin according to industry standards except that 40% of the phenol content was replaced by the NR. The resultant formulation was termed E-L-1-6. E-L-1-6 was compared with an commercially available PF resin (Tembec CL300), and E-K-4-6, a PF resin that prepared according to industry standards (Table 1) which contained 100% phenol, within OSB production.

Typical NR resin formulations involved loading phenol, water and paraformaldehyde into a kettle and heating to 95°C to dissolve the paraformaldehyde. The mixture was cooled to 45°C and the NR added. Caustic (NaOH) was then added to the desired pH thereby solubilizing the NR and initiating the reaction. During the addition of caustic, the mixture is maintained at 45°C for the first caustic addition (approximately 2/3 of the amount required). The mixture is then slowly heated to 90°C over a 30 min period over which time the resin is monitored for viscosity and

subsequently cooled prior during which the remaining caustic is added. The resin was maintained at 10°C until use.

**Table 1: comparison of properties of NR and phenol based resins**

5

Resin	Viscosity (cP)	pH	Caustic content	Resin Solids
NR: E-L-1-6	78.5	10.05	5.7	42.4
Control:E-K-4-6	130	10.41	5.7	41.8

10

The OSB's were prepared following standard industrial procedures using either E-L-1-6 (NR), with the pH adjusted to 10.4, E-K-4-6 (control) or CL300. The parameters for OSB production were as follows:

15	Strands:	3 inch poplar from an OSB mill
	Panel type:	homogenous
	Panel thickness:	7/16"
	Panel size:	18" x18"
	Resin content:	2.0%
20	Wax content:	1.5%
	Mat moisture:	5.5%
	Press time:	3 min or 4.5 min
	Press temperature:	215°C
	Replication:	4

25

The prepared OSB were tested for the following properties: density, IB (internal bond), MOR (modulus of rupture), and MOE (modulus of elasticity), according to the Canadian product standard for OSB (CSA 0437.1-93, April 1993):

30 The test results are presented in Table 2

**Table 2: Comparison of mechanical properties of panels prepared using formulation with 0% and 40% phenol replacement with NR Oil no 1.**

5	Resin			Press Cycle min	Density Kg/m <sup>3</sup>	MOR MPa		IB MPa	MOE MP
	Code	Phenol replacement	pH			Dry	Wet		
	E-L-1-6	40%	10.40	3.0	660	31.0	14.8	0.368	5554
	NR			4.5	660	33.6	16.0	0.445	5513
	E-K-4-6	0	10.41	3.0	662	32.5	14.8	0.427	5638
	Lab Control			4.5	660	34.4	16.6	0.468	5723
10	CL-300	0	10.34	3.0	664	36.5	15.6	0.515	5426
	Ind. Control			4.5	665	36.8	16.0	0.505	5776

15 Note: The pH of E-L-1-6 was adjusted to 10.40 prior to panel preparation.

Panels produced using a resin composition comprising non-optimized NR substituted for 40% of phenol, exhibited properties equivalent to that of the industrial PF resin composition for press times of 4.5 min. The OSB prepared using NR based resins did not exhibit any difference in appearance compared with OSB's prepared using PF resins.

25 Without wishing to be bound by theory, it is possible that the organic acid content of the NR based resin formulation may neutralize the caustic that is normally used to catalyse the condensation reaction used for the setting process of the OSB thereby requiring longer press times in order to ensure curing of the resin. These results indicate that a substantial proportion of phenol within PF resin formulations may be replaced with an NR fraction obtained from bio-oil.

**Example 3: NR-containing PF resin formulations - replacement of formaldehyde**

5       Due to the natural aldehydes present within NR, a reduction in the  
amount of formaldehyde within PF resin formulations comprising NR was examined.  
Results indicate that up to 20% of the formaldehyde can be replaced with NR and the  
OSB still maintains properties of control OSB's.

10       A control PF resin was formulated having a F/P molar ratio of 2.16:1.00.  
Several NR based resins were prepared by replacing 40% of the phenol (w/w) and  
having a F/P molar ratio of 2.16:1.00, 1.8:1.00 or 1.50:1.00. The properties of the  
different resins used are listed in Table 3, where the following NR's were used:

15       NR     - standard hardwood-derived NR  
NRP    - washed NR  
PO      - softwood-derived NR

**Table 3: Physical and Chemical Characteristics of Resins**

Material Code	Viscosity (cP)	Solid Content	Caustic Content (%)	pH After Caustic	Final pH	Gel Time (sec)	Free Phenol (%)	Free HCHO (%)	Molar Ratio (HCHO: Phenol)
PF Control	98.5	41.9	5.7	9.25	10.36	609	0.64	1.68	2.16:1.00
NR	226.5	43.5	8.02	9.1	10.28	507	non detected	7.18	2.16:1.00
NRP	73	41.4	5.7	8.85	9.92	485	non detected	10.17	2.16:1.00
NR	73	41.2	8.02	9.1	10.27	560	*	2.17	1.80:1.00
PO	79	42.6	8.02	*	10.19	873	*	0.86	1.50:1.00

\*=Data not available

OSB panels were prepared and tested as defined in Example 2 using CL300 (industry control), control, NR, NRP or PO based PF resin formulations defined in Table 3. Except that only a 3 min press time was used. The results of the tests are presented in Tables 4 and 5.

Table 4: Comparison of mechanical properties of panels prepared with NR replacement of phenol and formaldehyde (HCHO)

Material Code	Resin		Press Cycle mins	Density Kg/m3	MOR		IB MPa	MOE MPa	Thickness Swell %	Molar Ratio (HCHO: Phenol)
	Phenol replacement %				Dry	Wet				
CL300	NA		3	664	36.5	15.6	0.515	5426	NA	NA
Control	NA		3	665	31.6	14.9	0.450	4341	18.4	2.16:1.00
NR	40		3	652	27.9	11.5	0.340	4526	20.5	2.16:1.00
NR	40		3	653	29.2	14.8	0.468	4239	19.2	1.80:1.00

Table 5: Comparison of mechanical properties of panels prepared with NR Replacement of Phenol and formaldehyde (HCHO).

Resin Material Code	Phenol Replacement (%)	Press Cycle (mins)	Density (Kg/m <sup>3</sup> )	MOR		IB (MPa)	MOE (MPa)	Thickness Swell %	Molar Ratio (HCHO: Phenol)
				Dry	Wet				
PF Control	0	3.0	655	31.6	14.9	0.45	4341	18.4	2.16:1.00
NR	40	3.0	652	27.9	11.5	0.34	4526	20.5	2.16:1.00
NRP	40	3.0	665	34.1	15.4	0.45	4552	*	2.16:1.00
NR	40	3.0	653	29.2	14.8	0.47	4239	19.2	1.80:1.00
PO	40	3.0	642	27.5	13.8	0.42	4289	21.8	1.50:1.00

\*Data not available

From the results it can be seen that OSB's prepared using a F/P molar ratio of 1.80:1.00 gave equivalent results to that produced using PF resins with 3 min press times. Also, NRP-containing resins exhibit similar properties to that of commercially available PF resins. These results also indicate that softwood-derived non-optimized NR may also be used within PF resin formulations.

#### Example 4: PF resin formulations comprising NR

A series of PF resins were prepared with the compositions listed in Table 6. The base phenol-formaldehyde resin composition was a resol-type resin pH 11 with a P:F ratio of 2.5:1. The NR used in the sample preparations was obtained as described in Example 1.

----- Table 6: PF resin compositions

Sample	Phenolic resin % (w/w)	Quebracho tannin* % (w/w)	NR % (w/w)	Triacetone** % (w/w)	P:F ratio
A	100	0	0	2	2.5
B	81	0	19	2	2.5
C	62	0	38	2	2.5
D	40.5	40.5	19	2	1.6

\* quebracho tannin (273 g/mol monomeric molecular equivalent) was used as a natural phenolic additive.

\*\* triacetone was used as an accelerator of the resin.



These samples were used to prepare particle boards under the following conditions:

press temperature: 175°C  
maximum pressure: 30 Bar  
thickness: 9.0 mm  
press time: 15 s/mm  
degassing time: 30 sec.

The prepared panels exhibited the characteristics as disclosed in Table 7:

**Table 7: Characteristics of particle board panels prepared using the resins of Table 6.**

Sample	Internal bond (N/mm <sup>2</sup> )	Bending Strength (N/mm <sup>2</sup> )	Swelling * (%)	Density (Kg/m <sup>3</sup> )
A	1.30	22.5	15	830
B	1.30	22.1	26	830
C	1.15	21.0	45	825
D	1.25	22.0	32	825

\*measured after 24 hours soaking at 20°C

These results indicate that NR can be substituted for phenol, up to 40%, within PF resin compositions with no significant effect on internal bond or bending strength.

**Example 5:** Urea-formaldehyde resins formulated with NR.

A commercially available UF resin (L2600) produced by Rescol (Italy) was used having a 63% dry content, and a formaldehyde:urea ratio of 1.2:1.

This resin was used as a base resin for a series of UF formulations comprising NR, obtained as outlined in Example 1. Particle boards were prepared as defined in Example 6, with a total of 12% dry glue on dry wood. The resin compositions and test results are disclosed in Table 8. The amounts were calculated for dry resin and dry wood. The glue mixtures were all hardened with 1.5% ammonium sulphate.

**Table 8: UF Adhesive mixtures used, and mechanical characteristics of particle board prepared with the defined adhesive compositions.**

Sample	UF %*	NR %*	Internal Bond (n/mm <sup>2</sup> )	Bonding strength (n/mm <sup>2</sup> )	Swelling** %	Density (Kg/m <sup>3</sup> )
A	12	0	1.30	21.2	24	720
B	6	0	0.60	9.3	50	725
C	7.2	4.8	1.15	15.7	35	720
D	6	6	0.70	13.2	48	710

\* (w/w)

\*\*measured after 24 hours soaking at 20°C

The results of Table 8 demonstrate that with reduced amounts of UF (note: no added NR), several of the particle board characteristics deteriorate (compare A and B). However, the addition of NR (see D) enhances the characteristics observed within the UF-prepared panel. Furthermore, replacement of 40% of the UF within the resin formulation produces a similar particle board product as that prepared with UF resin.

**Example 6:** Testing of different NR's within PF adhesives at various formaldehyde mole ratios.

Several different NR preparations were tested within PF resin formulations. The NR's were obtained as outlined in Example 1, except that pine was used as the feedstock.

5 The formaldehyde:phenol molar ratio tested were 1.5:1 and 1.8:1, with 40% of the phenol replaced by NR. The characteristics of the PF resin formulations comprising NR are defined in Table 9.

**Table 9: Physical and chemical characteristics of resins**

10

	Viscosity (cP)	Solid content (%)	Caustic Content (%)	final pH	gel time (sec)	Molar ratio P:F
Control	126	42.1	5.7	10.31	518	2.16
E-H-2-7						
E-1-2-7	120	41.7	8.18	10.11	530	1.8
15 E-1-3-7	113	42.2	7.9	10.05	568	1.5
E-1-4-7	220	41.7	8.32	10.19	621	1.5
E-1-5-7	3260	41.6	7.49	10.22	335	1.8

20 The resin formulations of Table 9 were used for the production of OSB's under the following conditions:

25

Replications:	4 per press cycle
strands:	3 in poplar
support:	cauls
panel type:	homogeneous
thickness:	11.1 mm
resin content:	2.0%

MC%: 5.0%  
 press cycle: 3.0 min (includes 30 sec closing and 30 sec opening)  
 press temp: 215°C  
 wax: 1.5%

The boards were tested for internal bond strength (IB), modulus of rupture (MOR), modulus of elasticity (MOE), torsion shear (TS) and some panels were tested for thickness swelling (ThS). The results of these test are presented in Table 10.

**Table 10: effect of formaldehyde:phenol molar ratio on mechanical properties for a softwood NR (pine), and "conditioned NR".**

	Phenol	Density	MOR (MPa)		IB	MOE	TS	ThS
	(%)	(Kg/m <sup>3</sup> )			(MPa)	(MPa)	(in.lb)	(%)
			dry	wet				
Control	100	685	35.4	17.8	0.429	5483	30.5	n.d.
E-H-2-7								
E-1-2-7	60	680	34.3	16.1	0.387	5413	21.9	n.d.
E-1-3-7	60	680	42.8	15.1	0.340	6101	18.7	n.d.
E-1-4-7	60	680	35.4	14.4	0.378	5618	16.2	n.d.
E-1-5-7	60	680	27.7	11.5	0.325	4720	8.8	n.d.

The results of Table 10 demonstrate that PF resins, containing 40% NR derived from softwood (pine), at a formaldehyde:phenol ratio of 1.8:1 or 1.5:1, produces OSB's with comparable properties to OSB's prepared using commercial PF resin formulations with a formaldehyde:phenol ratio of 2.16:1.

## **Example 7 - Testing of NR60 with PF Adhesives**

Eleven 3' x 3' x 0.5" plywood panels were manufactured in order to evaluate the effects of varying concentrations NR60 substitution for phenol in PF resin.

5

### **1.0 Plywood Panel Manufacture**

#### **1.1 Blending and Forming**

10 Three different resin compositions were applied to pine veneers (Table 9). This resulted in three groups with a minimum of three panels per group. All applications were made at a 35 lb/1000 ft<sup>2</sup> loading rate. All resins were applied using a plywood glue spreader and applied on a single glue line.

15 Billet lay-up for each panel consisted of four plies. The face plies were laid-up parallel to the machine direction and the core plies were laid-up perpendicular to machine direction. Three control panels control four PF/NR60, at 10% panels (Group NR60-10%), and four PF/NR60 at 20% (Group NR60 - 20%) panels were manufactured in the trial.

20

#### **1.2 Pressing and Testing:**

25 Before pressing, the billets were pre-pressed (cold) at 150 psi for four minutes in a 4' x 8' press. The panels were then transferred for hot pressing to a 3' x 3' press. The panels were pressed under constant pressure control for 300 seconds at 300°F. Pressing was monitored and controlled with a PressMAN® Press Monitoring System.

30 After pressing, the panels were trimmed to 28" x 28" dimensions and hot stacked. Once cooled, the panels were evaluated. The panels were tested for plywood glue bond and flexural creep (CSA 0151-M1978).

### 1.3 Observations

No resin quality differences were noted visually during panel manufacture. The control and NR substituted resins behaved in the same manner with equal spreadability. The shear data suggests the NR substituted resin performed as well as the control (Table 10). The NR60 - 10% and NR60 - 20% resins both performed comparably to the control, under both test conditions with respect to shear strength. The resins showed exemplary strength characteristics with the ply only failing on the glue bond a maximum of 12% (PG2-88% average wood failure) under both test conditions. The strength of the NR-resin data is further supported by the fact not one sample demonstrated less than 60%, or less than 30#, wood failure under both test conditions.

Table 9

Group ID	No. of Panels	Resin Type	Resin Loading	Pressing Time (sec)
Control	3	GP PF Resin (Control)	35 lbs/1000ft <sup>2</sup> single glue line	300
NR60-10%	4	GP PF/NR 10 Resin	35 lbs/1000ft <sup>2</sup> single glue line	300
NR60-20%	4	GP PF/NR 20	35 lbs/1000ft <sup>2</sup> single glue line	300

**Table 10A** SUMMARY OF GEORGIA PACIFIC CONTROL AND GEORGIA PACIFIC NR RESIN PLYWOOD SHEAR TESTS: NR10 RESIN & NR20 RESIN

5

(Average values for ten specimens per panel from 3 panels per group)

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Test Condition	Property	CSA 0151 Requirement	Units	Control	NR 60 10%	NR60 20%
Vacuum-Pressure Soak:	Shear Strength	No. Req.	psi	89	102	88
	Percent Wood Failure Average	80	%	95	90	88
	Percent Wood Failure > =60	90	%	100	100	100
	Percent Wood Failure > =30	95	%	100	100	100
Boil-Dry Boil:	Shear Strength	No. Req.	psi	79	80	69
	Percent Wood Failure - Average	80	%	91	90	91
	Percent Wood Failure > =60	90	%	93	100	100
	Percent Wood Failure > =30	95	%	100	100	100

#### Introduction

#### Example 8. NR-60 used at 25% for the Preparation of Plywood and OSB Panels

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A total of seventeen 3' x 3' x 0.50" OSB, and fifteen 3' x 3' x 0.50" plywood panels were manufactured to evaluate the effects of 25% substitution of NR60 for phenol in PF resin, for both OSB and plywood.

## 1.0 OSB Panel Manufacture

### 1.1 Blending and Forming:

The resins were supplied by Neste in the following formats: Neste PF face control #1, Neste PF core control #2 and Neste PF/NR-60 - 25% (experimental). Three groups of panels were manufactured as indicated in Table 11. The control group (SNC) consisted of the Neste face control #1 resin applied to the strands along with commercial E-wax; the strands were then formed into random homogenous mats. The first experimental group (SNE) consisted for the substitution of the Neste PF/NR60 - 25% resin for the face control resin in the same manufacturing methodology. The final experimental OSB group (SN) utilized Neste PF/NR 60-25% on the panel face strands and the Neste core control #2 on the panel core strands. The SN mats were of 50/50 face-core random construction.

TABLE 11. PF AND PF-NR60 RESIN OSB TESTS

Group ID	No. of Panels	Resin Content	PANEL SPECIFICATIONS			
			Construction	Thickness (in.)	Density (lb/ft <sup>3</sup> )	Comments
SNC	8	Neste PF Face resin, 3.5% (Control #1)	Homogenous	0.5	39	OSB control
SNE*	6	Neste PF/NR 25, 3.5%	Homogenous	0.5	39	OSB Trial



SN**	3	Face: Neste PF/NR 25, 3.5% Core: Neste PF core resin, 3.5% (Control #2)	50/50 face- core	0.5	39	Face NR Substitute Core Control on OSB
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\* NR/RF resin used on the surface and core of the OSB

\*\* NR/PF resin used on surface only

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All resins were applied at a 3.5% solids basis. The commercial e-wax was applied at a 1.0% solids basis. All billets were hand formed to yield a density of 39 lb/ft<sup>3</sup> when pressed to a thickness of 0.5".

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## 1.2 Pressing and Testing:

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After formation, the mats were then pressed utilizing a standard OSB pressing cycle. The total pressing time was set to a conservative 400-second cycle to ensure complete cure of the applied resin. Pressing was monitored and controlled with a PressMAN® Press Monitoring System.

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After pressing, the panels were removed, trimmed to 28" x 28" dimensions, then measured for out-of-press thickness and density.

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After the measurements were made, the panels were hot-stacked. Upon cooling, the panels were tested to CSA of 0437.2 - 93 for: MOR/MOE, IB, bond durability (2hr and 6hr cycles), thickness

swell (24hr soak), and linear expansion (ODVPS) as well as flexural creep.

## **2.0 Plywood Panel Manufacture**

### **5                    2.1    Glue Spreading and Veneer Lay Up**

The plywood portion of the study involved the gluing and lay up of commercial pine veneers. Two plywood resins were used for the study. The first resin was identified as the Neste PF (plywood control) while the second was identified as Neste PF/NR 25 (plywood experimental).

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The resins were applied to the veneers using a glue spreader. A rate of 35 lbs.per 1000ft<sup>2</sup>, applied on a single glue line was utilized. The lay up consisted of two face veneers, parallel to machine direction, and two core veneers, perpendicular to machine direction, for each panel. Eleven control (Group PNC) and four experimental (Group PNE) panels, were manufactured (Please refer to Table 12).

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TABLE 12 PF AND NR60 RESIN PLYWOOD SHEAR TESTS

Group ID	No. of Panels	Resin Content	PANEL SPECIFICATIONS			
			Construction	Thickness (in.)	Density (lb/ft <sup>3</sup> )	Comments
PNC Control	11	35lb/m SGL Neste PF (plywood)	Four ply pine Veneers	0.5	-	Plywood control
PNE (25% NR)	4	35lb/m SGL Neste PF/NR (plywood)	Four ply pine Veneers	0.5	-	Plywood test resin

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During lay up, gluing time, open assembly time, pre-pressing time and closed assembly time were measured for each panel.

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## 2.2 Pressing and Testing

5 After pre-pressing at four minutes and 150 psi, the billets were placed in a press for final cure and pressing. The first seven control panels (PNC 1-7) were used to establish the pressing time. This resulted in the establishment of 300 seconds as the required pressing time. Pressing was monitored and controlled via a PressMAN® Press Monitoring System.

10 After pressing, the panels were then trimmed to 28" x 28" dimensions then hot stacked. Upon cooling, the panels were evaluated. Testing consisted of glue-bond shear and flexural creep evaluation.

## 15 3.0 Observations and Results

Virtually no difference was observed between the control and NR substitution resins. Color, viscosity and spreadability for all resins seemed equal. A slightly different odor was noted in the NR resins versus the controls. 20 This odor did not prove to be pervasive or intrusive however. Otherwise, all resins appeared to behave equally in a manufacturing situation.

A comparison of the NR substituted resins versus the control (SN, SNE, vs. SNC) show bending and bond properties to be equal between the three 25 groups (Table 13). The results indicate, especially with group SN, a drop in bond durability and linear expansion versus the control. Group SN showed a value of water swell well within the maximum requirement.

Table 13 SUMMARY OF PF AND PF/NR60 25% OSB TESTS

Property	Requirement	Units	Control Group (SNC)	NR Surface/Neste Core (SN)*	NR Surface/NR Core (SNE)**
Modulus of Rupture (after pre-conditioning)	Min. 2500	psi	3210	3190	3190
Modulus of Elasticity (after pre-conditioning)	Min. 450	psi x 1000	479	493	469
Internal Bond (after pre-conditioning)	Min. 50.0	psi	56.3	49.7	54.6
Bond Durability - MOR after 2HR.					
BOIL (tested when wet)	Min. 1250	psi	1760	1310	1420
- MOR after 6 cycle	Min. 1250	psi	2270	1550	1870
Thickness Swell - 24 hour Soak	Min. 25	%	16.6	21.2	17.6
Lin. Expansion - O.D. to saturated	Max. 0.40	%	0.36	0.41	0.43
- 50%-90% R.H.	Max. 0.20	%	0.18	0.25	0.21

\* NR/PF resin used on surface only

\*\* NR/RF resin used on the surface and core of the OSB

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With respect to the plywood shear testing the results were favourable both against the standard and the control Group (Table 14). A strong bond was indicated by the shear strength performance under both test conditions. Under both conditions 11% or less failure could be attributed to the glue while the maximum allowable is 20% (89% wood failure for Group PNE under boil-dry-boil). A further indicator in the strength of the data was that not one PNE sample showed wood failure values of less than 60% or 30% under both test conditions (100% pass for both requirements on both test regimens).

**Table 14 SUMMARY OF PF AND PF/NR60 - 25% RESIN PLYWOOD SHEAR TESTS**

Test Condition	Property	CSA 0151 Requirement	Units	Control Group (PNC)	Neste NR/PF (PNE)
Vacuum-Pressure Soak:	Shear Strength	No. Req.	psi	82	110
	Percent Wood Failure Average	80	%	87	93
	Percent Wood Failure $\geq 60$	90	%	93	100
	Percent Wood Failure $\geq 30$	95	%	100	100
Boil-Dry Boil:	Shear Strength	No. Req.	psi	74	83
	Percent Wood Failure Average	80	%	89	89
	Percent Wood Failure $\geq 60$	90	%	100	100
	Percent Wood Failure $\geq 30$	95	%	100	100

**Example 10. Use of NR60 at 40% in the production of OSB panels**

5 An experimental resin formulation was used to prepare four 40% phenol substitution resins using NR60 (formaldehyde to phenol ratio 1.6:1) from four different samples (labelled NR60-D, NRB 166, 1°CT, and CALCT). A lab control was also prepared and used as reference for the evaluation of all experimental resins. NRB is an NR60 obtained from bark.

10 The performance of the formulated resins has been evaluated by testing the mechanical properties such as internal bond strength (IB), modulus of elasticity (MOE), modulus of rupture (MOR, dry and wet), torsion shear, thickness swelling and water absorption from 20 OSB panels manufactured with the five resins. All the resins were characterised using several standard best methods such as solids content, viscosity, pH, gel time and free formaldehyde.

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**Panel general parameters:**

Replicates: 4  
Strands: 3-in, poplar  
Support: screen  
20 Panel type: homogenous  
Thickness: 11.1 mm  
Target density: 640 kg/m<sup>3</sup>  
Press temp: 215°C  
Press cycle: 3.0 min  
25 Moisture content: 5.0%  
Wax content: 1.5%  
Resin content: 2.0%

## Test Results

5 Table 15 shows the physical and chemical characteristics of the resins formulated from the different NR60 - 40% samples (NR60-D, NRB 166, 1°CT and CALCT). The results obtained with the phenol/formaldehyde control are included for comparison. In every case, the resin formulated with NR60 needed 1.5 to 2.2% more caustic catalysts to produce a resin with an equivalent pH to the control. The pH and viscosity values of E-F-4-8 and E-F-5-8 resins are similar to the control but show less advanced characteristics for E-F-2-8, 10 and E-F-3-8. The same factor applies to the gel time obtained with the four experimental resins even if it takes longer than the lab control value.

15 Table 16 summarizes the OSB test results for E-F-2-8 (NR60-D), E-F-3-8 (1°CT), E-F-4-8 (CALCT) and E-F-5-8 (NRB166), compared to E-F-1-8 (lab control).... Results regarding the internal bond and the torsion shear are lower than the control. MOE and MOR values (dry and wet) are similar to the control. For thickness swell and water absorption, except E-F-4-8 (CALCT) that gives better values, results were also lower than for the control.

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## Conclusion

Of all the resins E-F-4-8 (CALCT oil) gave the best results. The other three had lower results in almost every test.

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Table 15 Physical and chemical characteristics of the resins E-F-1-8, E-F-2-8, E-F-3-8, E-F-4-8 and E-F-5-8

	Viscosity (CP)	Solid Content (%)	Caustic Content (%)	pH After Caustic	Final pH	Gel Time (s)	Free HCHO (%)	Molar Ratio
E-F-1-8 Control	42.0		5.70	9.50	10.16	559	1.33	2.16:1.0
E-F-2-8 NR60-D	65	41.0	7.66	9.41	10.04	626	0.45	1.6:1.0
E-F-3-8 1°CT	55	42.0	7.16	9.50	10.06	658	1.16	1.6:1.0
E-F-4-8 CALCT	90	42.3	7.40	9.49	10.15	607	1.66	1.6:1.0
E-F-5-8 NRB166	80	41.4	7.89	9.53	10.14	608	0.58	1.6:1.0

Table 16: Mechanical properties of the resins E-F-1-8, E-F-2-8, E-F-3-8, E-F-4-8 and E-F-5-8

Code	Resin Phenol Replace. (%)	Press Cycle (min)	Density (Kg/m <sup>3</sup> )	MOR (MPa)		MOE (MPa)	I.B. (MPa)	Torsion Shear Wet (in lb.)	Thickness Swelling 24 hrs (%)	Water Absorption 24 hrs (%)
				Dry	Wet					
E-F-1-8 Control	0	3.0	676	22.9	14.7	5818	0.481	35.1	19.2	38.0
E-F-2-8 NR60-D	40	3.0	679	22.8	1.4	4424	0.44	19.1	19.9	37.2
E-F-3-8 1°CT	40	3.0	682	23.2	13.5	4835	0.44	23.4	21.0	37.3
E-F-4-8 CALCT	40	3.0	692	25.5	14.1	5875	0.472	22.5	18.6	34.7
E-F-5-8 NRB 166	40	3.0	680	21.4	15.3	5406	0.414	17.2	20.8	39.0

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The present invention has been described with regard to preferred embodiments. However, it will be obvious to persons skilled in the art that a number of variations and modifications can be made without departing from the scope of the invention as described herein.

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**THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OF PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:**

1. A natural resin (NR) characterized by comprising:
  - i) a free phenol content from about 0.001 % to about 0.1 % (w/w);
  - ii) a total phenolic content from about 30% to about 80% (w/w); and
  - iii) a pleasant smoky odour.
2. The NR of claim 1 further characterized by comprising
  - i) a pH from about 2.0 to about 3.0;
3. The NR of claim 1 further characterized by comprising:
  - i) a water content of from about 10 to about 20 wt%;
  - ii) a density from about 1.0 to about 1.3 g/ml;
  - iii) a solid content from about 0.5 to about 1.0 wt%;
  - iv) an ash content from about 0.05 to about 0.5 (wt%);
  - v) a viscosity at 75°C from about 70 to greater than 300 (cSt); and
  - vi) a pH from about 2.0 to about 7.
4. The NR of claim 3 further characterized by comprising:
  - i) a net caloric value of about 4355 cal/g (18.22 MJ/kg); and
  - ii) a gross caloric value of about 4690 cal/g (19.62 MJ/kg).
5. An adhesive composition comprising the NR of claim 1.
6. The adhesive composition of claim 5 wherein the NR is present within said adhesive composition from about 1 % to about 40 % (w/w).
7. The adhesive composition of claim 6 further comprising a second adhesive resin selected from the group consisting of a phenol-containing formaldehyde resin, and a urea-containing formaldehyde resin.

- 8 The adhesive composition of claim 7 wherein the second adhesive resin is phenol formaldehyde.
9. The adhesive composition of claim 7 wherein the second adhesive resin is urea formaldehyde.
10. The adhesive composition of claim 8 wherein the NR comprises from about 10 to about 40% (w/w) of said adhesive composition.
11. The adhesive composition of claim 9 wherein the NR comprises from about 20 to about 60% (w/w) of said adhesive composition.
12. The adhesive composition of claim 7 wherein a portion of the formaldehyde of either the phenol-containing formaldehyde resin, or urea-containing formaldehyde resin is replaced with NR.
13. The adhesive composition of claim 12 wherein NR replaces up to about 50% of the formaldehyde content within the phenol-containing formaldehyde resin, or urea-containing formaldehyde resin .
14. The adhesive composition of claim 12 comprising a formaldehyde:phenol ratio from about 1.5:1 to about 10:1.
15. The adhesive composition of claim 14 wherein the formaldehyde:phenol ratio is from about 2.5:1 to about 1.5:1.
16. The adhesive composition of claim 15 wherein the formaldehyde:phenol ratio is 1.8:1.
17. A wood product prepared using the adhesive composition of claim 5.

18. The wood product of claim 17, wherein the wood product is selected from the group consisting of laminated wood, plywood, particle board, high density particle board, oriented strand board, medium density fiber board, hardboard or wafer board.
19. The wood product as claimed in claim 18, wherein the wood product is for exterior applications.
20. A method of preparing a natural resin comprising:
  - i) liquefying wood, wood bark or other biomass using fast pyrolysis in order to produce product vapours and char;
  - ii) removing the char from the product vapours;
  - iii) removing a first set of components from the product vapours by rapid quenching, producing a remaining selected product vapour;
  - iv) obtaining the natural resin from the remaining selected product vapour.
21. The method of claim 20 wherein, the natural resin is obtained from the selected product vapour using direct-liquid contact condensers.
22. The method of claim 21 wherein the natural resin is obtained from a secondary condenser, a demister and a filter bed.
23. A natural resin prepared following the method of claim 20.
24. An adhesive prepared using the natural resin of claim 23.
25. The natural resin of claim 1, wherein the natural resin is washed.
26. The natural resin of claim 26, wherein the pH is greater than 3, and the phenolics comprise up to about 80% (dry wt%).

27. A natural resin mixture comprising a combination of the natural resin of claim 1 and a washed natural resin.
28. The natural resin mixture of claim 27, wherein the natural resin mixture is NR50.
29. An adhesive composition comprising the washed natural resin of claim 25.
30. The adhesive composition of claim 29, wherein the washed natural resin replaces up to about 100% of the phenol content of the resin.
31. An adhesive composition comprising the natural resin mixture of claim 27.
32. A wood product prepared using the adhesive composition of claim 29.
33. A wood product prepared using the adhesive composition of claim 31.



## ABSTRACT OF THE DISCLOSURE

This invention is directed to a method of preparing a natural resin by liquefying wood, bark, forest residues, wood industry residues, or other biomass using fast pyrolysis in order to produce product vapours and char. Following removal of the char from the product vapours, a first set of compounds are removed from the product vapours by rapid quenching in order to obtain a remaining selected product vapour from which a natural resin is obtained. The natural resin comprises a total phenolic content from about 30% to about 80% (w/w), and is further characterized as having a pleasant smoky odour. The natural resin has surprisingly been found to be suitable for use within adhesive formulations without requiring any further extraction or fractionation procedures. Adhesives comprising up to 60% natural resin have been prepared and tested in board production and found to exhibit similar properties associated with commercially available resins. The natural resin may substitute for phenol, or for both phenol and formaldehyde within phenol-containing resins. Similarly, the natural resin can replace a substantial part of the components within urea-containing resins.



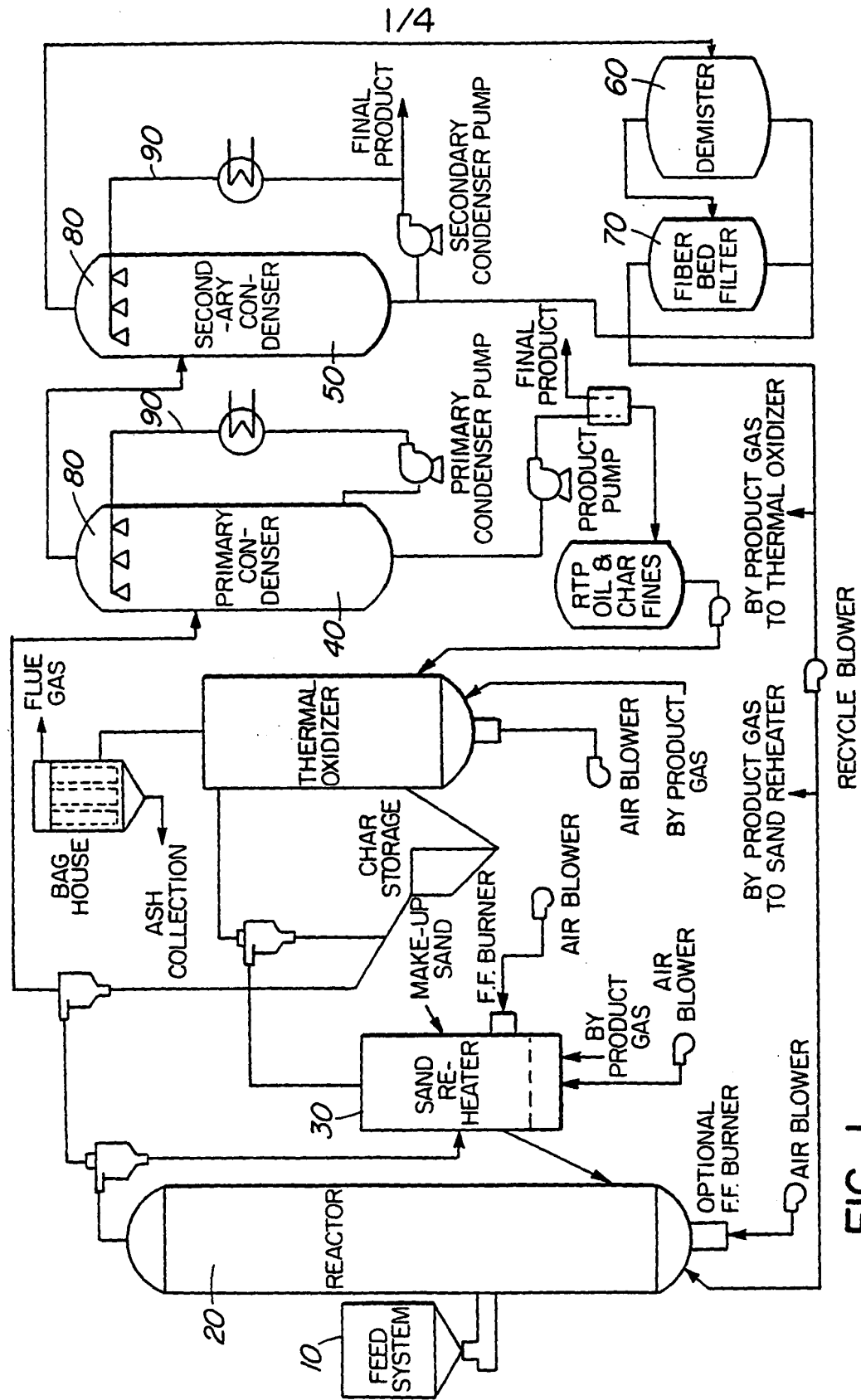


FIG. 1



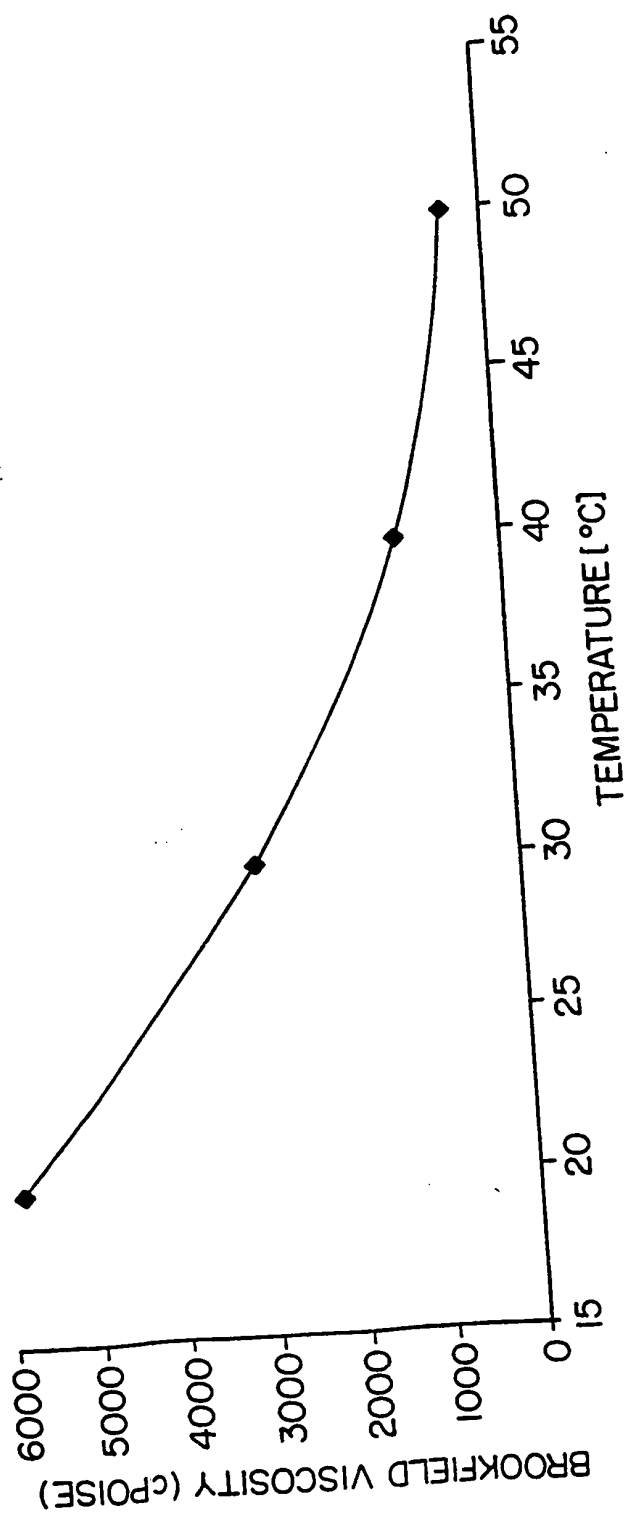


FIG. 2



3/4

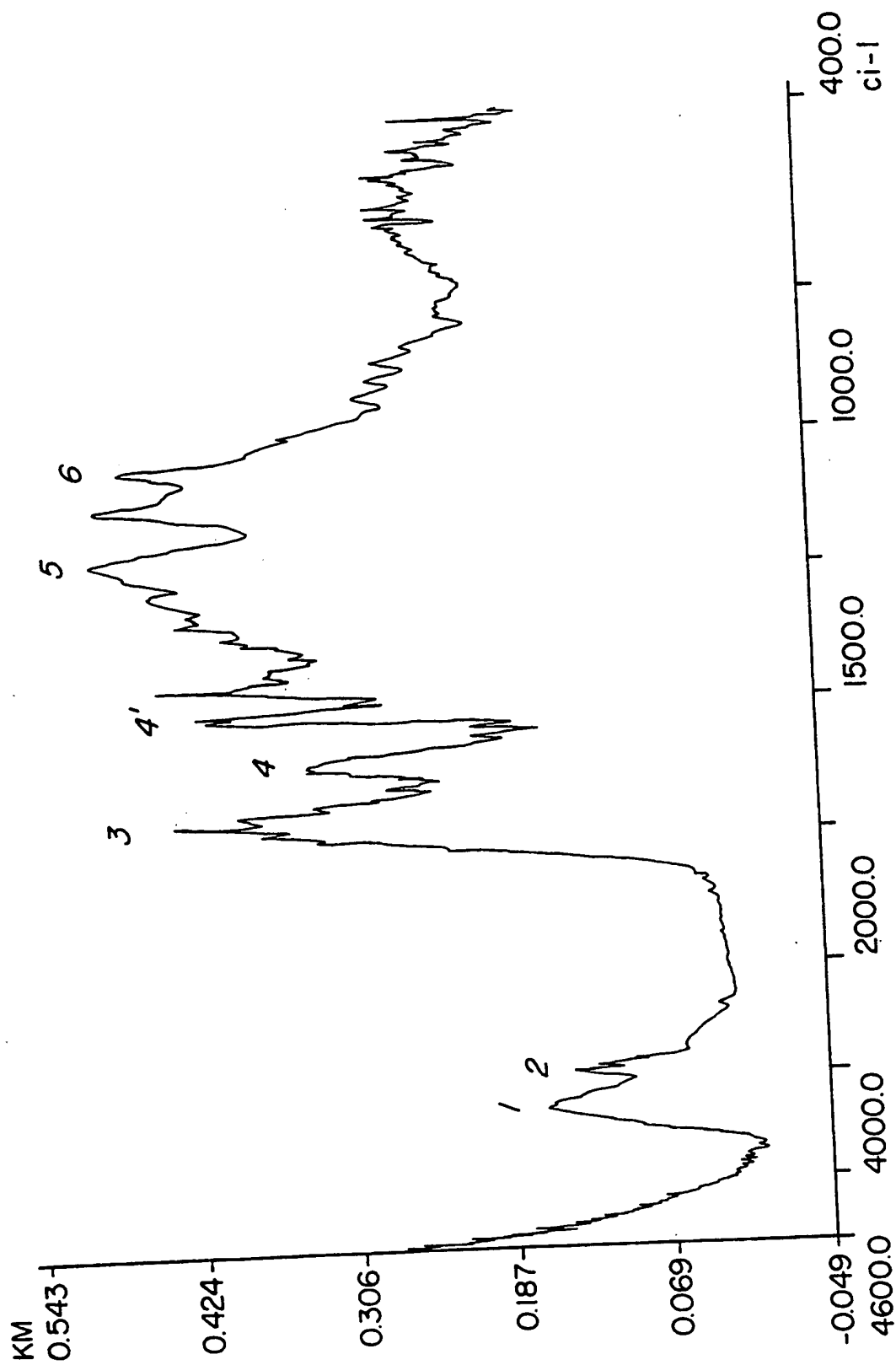


FIG. 3A





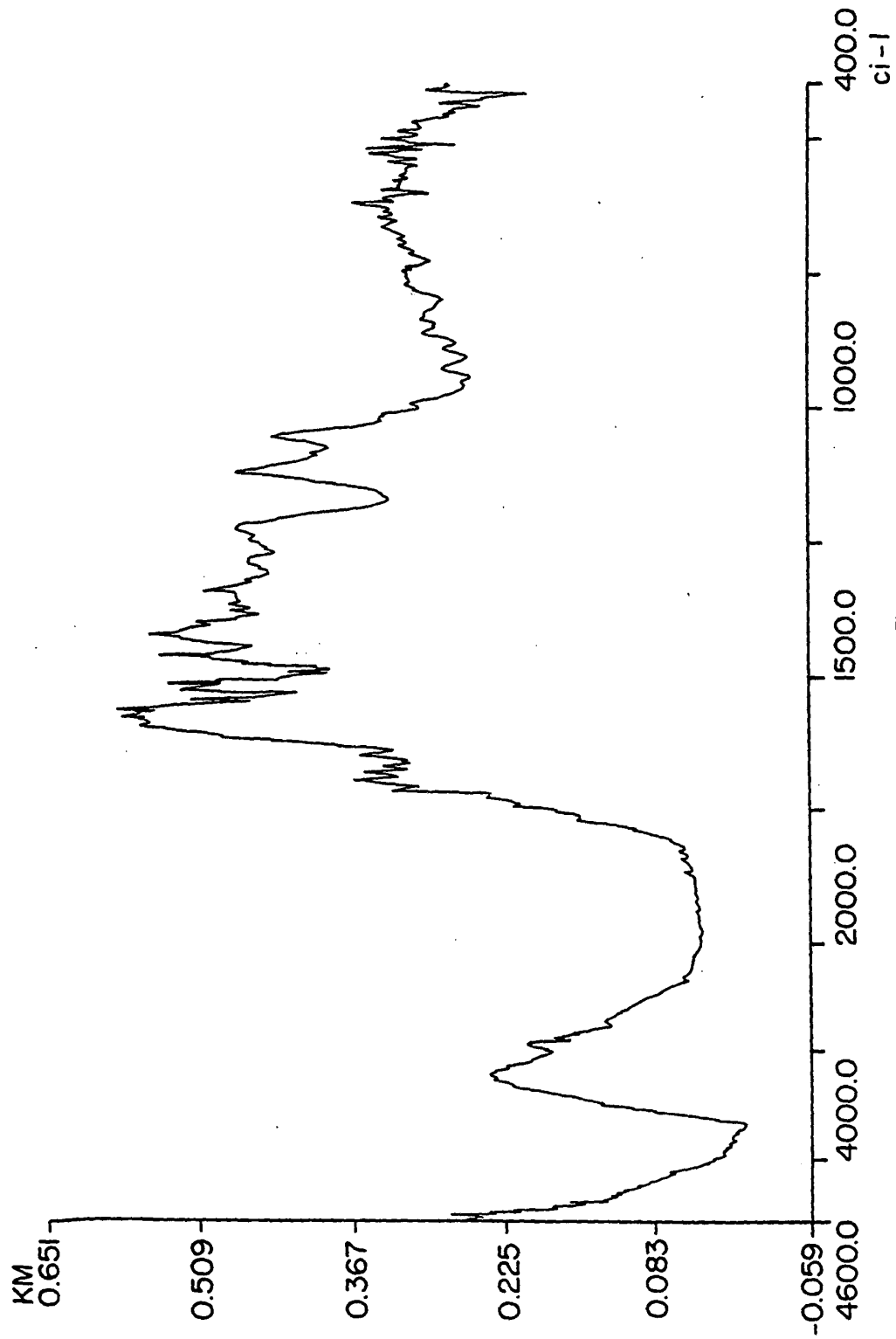


FIG. 3B



## PATENT COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

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Date of mailing (day/month/year) 05 April 2001 (05.04.01)	
International application No. PCT/CA00/00868	Applicant's or agent's file reference 08-878545WO1
International filing date (day/month/year) 28 July 2000 (28.07.00)	Priority date (day/month/year) 29 July 1999 (29.07.99)
Applicant FREEL, Barry et al	

1. The designated Office is hereby notified of its election made:

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# PCT REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.	00/00868
International Filing Date	28 JUL 2000 (28.07.00)
Name of receiving Office and "PCT International Application"	
Applicant's or agent's file reference (if desired) (12 characters maximum)	
O8-878545WO1	

<b>Box No. I TITLE OF INVENTION</b>	
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State (that is, country) of nationality: CA	State (that is, country) of residence: CA
<p>This person is applicant for the purposes of:</p> <p><input type="checkbox"/> all designated states      <input type="checkbox"/> all designated States except the United States of America      <input checked="" type="checkbox"/> the United States of America only      <input type="checkbox"/> the States indicated in the Supplemental Box</p>	
<p>Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</p>	<p>This person is:</p> <p><input type="checkbox"/> applicant only</p> <p><input type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only (If this check-box is marked, do not fill in below.)</p>
State (that is, country) of nationality:	State (that is, country) of residence:
<p>This person is applicant for the purposes of:</p> <p><input type="checkbox"/> all designated states      <input type="checkbox"/> all designated States except the United States of America      <input type="checkbox"/> the United States of America only      <input type="checkbox"/> the States indicated in the Supplemental Box</p>	
<p>Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</p>	<p>This person is:</p> <p><input type="checkbox"/> applicant only</p> <p><input type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only (If this check-box is marked, do not fill in below.)</p>
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☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.





## Box No. V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; at least one must be marked):

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| <input checked="" type="checkbox"/> <b>BA</b> Bosnia and Herzegovina                | <input checked="" type="checkbox"/> <b>MG</b> Madagascar                                    |
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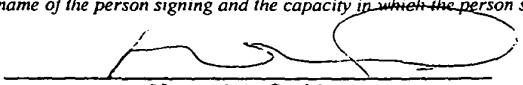
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**Continuation of box No. V.**

*This application claims priority from US patent application 09/364,610; Filed July 29, 1999 which is a CIP of PCT/CA99/00051, designating the US and for which an application was filed within the US on July 30, 2000, which claims priority from CA 2,228,418; Filed January 30, 1998.*



Box No. VI PRIORITY CLAIM		<input type="checkbox"/> Further priority claims are indicated in the Supplemental Box		
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application country	regional application: * regional Office	international application: receiving Office
item (1) 29 July 1999 (29.01.99)	09/364,610	US		
item (2)				
item (3)				
<input type="checkbox"/> The receiving Office is hereby requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s): _____				
<p>* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.</p>				
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Box No. VIII CHECK LIST; LANGUAGE OF FILING				
This international application contains the following number of sheets:  request : 5  description (excluding sequence listing part) : 64  claims : 4  abstract : 1  drawings : 6  sequence listing part of description : _____  Total number of sheets : 80		This international application is accompanied by the item(s) marked below:  1. <input type="checkbox"/> fee calculation sheet 2. <input type="checkbox"/> separate signed power of attorney 3. <input type="checkbox"/> copy of general power of attorney; reference number, if any: 4. <input type="checkbox"/> statement explaining lack of signature 5. <input type="checkbox"/> priority document(s) identified in Box No. VI as item(s): 6. <input type="checkbox"/> translation of international application into (language): 7. <input type="checkbox"/> separate indications concerning deposited microorganisms or other biological material 8. <input type="checkbox"/> nucleotide and/or amino acid sequence listing in computer readable form 9. <input type="checkbox"/> other (specify): _____		
Figure of the drawings which should accompany the abstract: <u>2A</u>		Language of filing of the international application: <u>ENGLISH</u>		
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Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).  <div style="text-align: center;">   <b>Konrad A. Sechley</b>          Patent Agent          Gowling Lafleur Henderson LLP       </div>				

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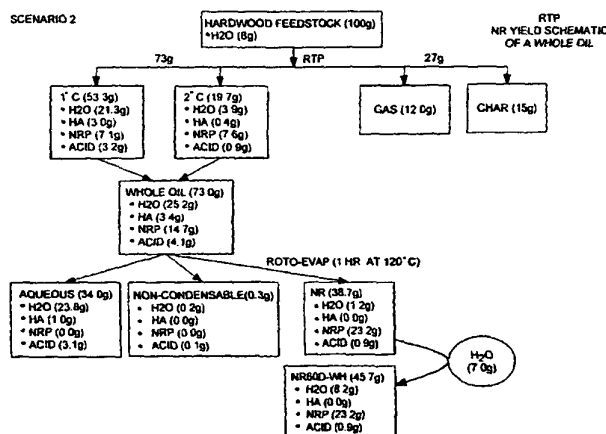
(74) Agents: SECHLEY, Konrad, A. et al.; Gowling Lafleur Henderson LLP, Suite 2600, 160 Elgin Street, Ottawa, Ontario K1P 1C3 (CA).

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[Continued on next page]

(54) Title: NOVEL NATURAL RESIN FORMULATIONS



(57) Abstract: This invention is directed to a method of preparing a natural resin by liquefying wood, bark, forest residues, wood industry residues, or other biomass using rapid destructive distillation (fast pyrolysis). Fast pyrolysis produces both vapours and char from biomass, and following removal of the char from the product vapours, a liquid pitch product is recovered and processed by distillation, evaporation, or a combination thereof, in order to obtain a natural resin which may be in either liquid or solid form. The natural resin comprises a total phenolic content from about 30 % to about 80 % (w/w), and is a highly-reactive ligninic compound that has been found to be suitable for use within resin formulations without requiring any further extraction or fractionation procedures. Resins comprising up to 60 % natural resin have been prepared and tested in board production and found to exhibit similar properties associated with commercially available resins. The natural resin may substitute for phenol, or for both phenol and formaldehyde within phenol-containing resins. Similarly, the natural resin can replace a substantial part of the components within urea-containing resins.







IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

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**Published:**

— *With international search report.*



## NOVEL NATURAL RESIN FORMULATIONS

The present invention relates to the production and use of a natural resin, derived from wood, bark, forest residues, wood industry residues and other biomass materials using destructive distillation, its use as an adhesive in the manufacture of manufactured wood products, and its use in other resin formulations.

### BACKGROUND OF THE INVENTION

"Resin" is a generic term used to describe both natural and synthetic glues which derive their adhesive properties from their inherent ability to polymerize in a consistent and predictable fashion. The vast majority of modern industrial resins are synthetic, and are normally derived from petroleum feedstocks. Two of the most important classes of synthetic resins, in terms of production volume and total sales are phenol formaldehyde (P/F) and urea formaldehyde (U/F) resins. In both cases, the principal market application is for use as a glue binder in man-made wood products.

Phenol formaldehyde (P/F) resin, because of its resistance to moisture, has a particular value in external (outdoor) or damp environments. It is therefore, the leading adhesive used for the manufacture of plywood, oriented strand board (OSB) and wafer board (Sellers, 1996). P/F resins are also widely used in laminates, insulation, foundry materials, moulding compounds, abrasives and friction materials for the transportation industry (ie., clutch facings, disk facings and transmission components). As its name suggests, the principal ingredients in P/F adhesives are phenol and formaldehyde. However, the finished product is actually a mixture of P/F, caustic, and water,. Assorted fillers, extenders and dispersion agents may then be added for specific adhesive applications.

The formaldehyde ingredient in P/F resin is derived from methanol, normally produced from natural gas. The phenol ingredient is typically manufactured from benzene and propylene via a cumene intermediate. In addition to P/F adhesive manufacture, phenol is used in the manufacture of other important products, for example, Bisphenol A and Caprolactam. Bisphenol A is a principal component in polycarbonates

used in automotive parts, compact discs and computer discs, and Caprolactam is a raw material for Nylon 6, used within stain resistant carpets.

When mixed together in water and with caustic added as a catalyst, phenol and formaldehyde undergo a condensation reaction to form either ortho- or para-methylolphenol. The resultant PF resin, as shipped to market, is a dark brown liquid which is polymerized and cross-linked to an intermediate degree. It is then cured in the final board, laminate or other product without catalyst simply with the addition of heat at which time the final polymerization and cross-linking take place via condensation reactions. The release of free formaldehyde during the resin manufacture and resin use stages is a concern from a health and safety perspective. Furthermore, the costs associated with formaldehyde production have increased and there is a need in the art for alternative materials for use as wood adhesives and binders.

One alternative for phenol that has been considered are lignins which have been recovered from wood, wood residues, bark, bagasse and other biomass via industrial or experimental processes. Natural lignin (i.e. the polymer which occurs in nature which holds wood and bark fibres together and gives wood its strength) and P/F formaldehyde resins are structurally very similar. Lignin is a random network polymer with a variety of linkages, based on phenyl propane units. Lignin-based adhesive formulations have been tested for use within plywood, particle board and fibre board manufacture. The addition of polymeric lignin to P/F formulations has been found to prematurely gel the P/F resin thereby reducing shelf life, limiting permeation of the lignin-P/F resin into the wood and producing an inferior mechanical bond (Kelley 1997). It is important to note that lignins which are isolated and recovered from biomass, and which have been tested in resin formulations, are not identical to the natural lignin present in the original biomass, but are altered somewhat by the recovery process. Some examples of recovered lignins which have been tested in PF resin formulations are Kraft lignin, lignosulphonates, Alcell™, Organocell™, pyrolytic lignin and natural resin of the present invention.

Pyrolysis of lignin has been considered as a potential approach to upgrading lignin to more usable phenolic type resins. While relatively mild thermal or thermocatalytic processing at low pressures can be used to break the lignin macromolecules into

smaller macromolecules, lignin segments and monomeric chemicals, such procedures may cause condensation reactions producing highly condensed structures such as char and tar, rather than depolymerized lignin fragments or monomeric chemicals.

5           A further alternative for the production of phenolic compounds involves use of  
pyrolytic pitch oils produced in the rapid destructive distillation (fast pyrolysis) of wood  
and other biomass. Fast pyrolysis can be achieved by rapid heat transfer to the feed  
material, by rapid removal of the product via a vacuum, or by a combination of rapid heat  
transfer and pyrolysis under vacuum. These pitch oils are comprised of a complex  
10       mixture of compounds including phenolic compounds, guaiacol, syringol and para  
substituted derivatives, carbohydrate fragments, polyols, organic acids, formaldehyde,  
acetaldehyde, furfuraldehyde and other oligomeric products (Pakdel et al 1996).  
However, wood-derived lignin and lignin-rich pyrolytic bio-oils have lacked consistency  
and have exhibited inferior properties when compared with phenol-formaldehyde resins  
15       (Chum et al. 1989; Scott 1988; Himmelblau 1997; Kelley et al., 1997).

Due to the complexity of pyrolytically-derived bio-oils, further processing is  
required in order to obtain suitable fractions useable as a replacement for phenol, or to  
be considered as an extender for petroleum-derived phenol within P/F resin formulations.  
20       Typically the phenolic derived from pyrolysis oils requires separation prior to use in  
order to remove impurities. One such method involves water extraction of the whole-oil,  
followed by precipitation and centrifugation or filtration and drying of the non-aqueous  
fraction to prepare a "pyrolytic lignin" fraction (Scott 1988). However, adhesive  
formulations prepared using pyrolytic lignin were found to be inferior to P/F resin  
25       formulations in both colour and odour, and required long press times in order to avoid  
de-lamination of waferboards. Tests indicated that none of the pyrolytic lignin samples  
meet the internal bond (IB) test requirement (Scott 1988, see pp. 91-92).

In US 4,209,647 (June 24, 1980) a fractionation method for the preparation of  
30       a phenol- enriched pyrolytic oil is disclosed which involved a multistep process that  
selectively solubilized neutral phenols, and organic acids of the whole-oil with NaOH  
followed by extraction with methylene chloride. However, this multistep process is  
costly, labourious, time consuming and involves the use of volatile solvents that are  
known to be health threatening.

Another fractionation method involves adding ethyl acetate to whole-oil pitch to produce ethyl acetate soluble and insoluble fractions. The ethyl soluble fraction is then isolated and the ethyl acetate evaporated to isolate a fraction containing phenolic and neutrals (P/N) derived from the pyrolytic oil (Chum et al. 1989, US Patents 4,942,269, 5  
July 17, 1990, and 5,235,021, August 10, 1993). Preliminary results with the P/N fractions revealed that fractionated pyrolytic oils could be used within P/F resin compositions, as P/N containing resins exhibited equivalent gel times as noted for P/F resins. However, the fractionation protocol is not suitable for industrial scale production, nor is this process cost effective for the preparation of alternative components for use  
10 within P/F resins at a commercial scale (Kelley et al., 1997).

All of the process disclosed within the prior art as outlined above involve the extraction of a phenol-enhanced fraction from the whole pyrolytic oil product using complex protocols involving precipitation, followed by centrifugation or filtration, or  
15 the use of solvents and alkali. None of the prior art discloses methods for the production of a bio-oil which is readily prepared from the whole pyrolytic oil or that exhibits properties suitable for adhesive use. Furthermore, the prior art does not disclose methods directed at producing a fraction of bio-oil suitable for adhesive use, yet that is simple to produce and that does not require any solvent extraction.

20

It is an object of the invention to overcome disadvantages of the prior art.

The above object is met by the combinations of features of the main claims, the sub-claims disclose further advantageous embodiments of the invention.

25

## SUMMARY OF THE INVENTION

The present invention relates to the production and use of a natural resin, a highly reactive ligninic product, derived from wood, bark and other biomass residues using rapid  
30 destructive distillation, for example, fast pyrolysis. Specifically, the natural resins (NR) of this invention are obtained from the fast pyrolysis of wood products. The NR is obtained from a ligninic fraction of the liquid pitch product produced from fast pyrolysis of biomass.

- 5 -

By the processes of the present invention, there is no need to extract a phenol enhanced portion using solvents, water induced solids separation, or alkali. Rather the NR of this invention may be produced from a selected product fraction of the whole-oil obtained from the pyrolytic process, or from the whole-oil product. The whole-oil, selected product fraction, or a combination thereof, is processed in a manner that reduces non-resin components including odorous components and acids in order to produce NR. Such a processing step involves distillation/evaporation.

The natural resins (NR) of the present invention can be used as a substitute for some of the phenol in phenol/formaldehyde, phenol urea formaldehyde, and phenol melamine urea formaldehyde resins used as adhesives in the manufacture of wood products, or the NR can be used as a substitute of some of the phenol and some the formaldehyde components of phenol-containing formaldehyde resins, for example industrial phenol-formaldehyde resins. Furthermore, the NR of this invention can be used as a substitute within urea formaldehyde resins, and melamine urea formaldehyde, and related resins. The natural resins of the present invention can be used as a substitute for either some of the phenol component of a phenol-containing formaldehyde resin or for both the phenol and formaldehyde components of the resin, or as a substitute within urea formaldehyde type resins.

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The natural resins of the present invention exhibit high reactivity due to the presence of a high number of active sites for binding and cross linking during polymerization.

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According to the present invention there is provided a method of preparing a natural resin (NR) comprising:

- i) thermally converting a suitable biomass via rapid destructive distillation in order to produce vapours and char;
- ii) removing the char from the vapours;
- 30 iii) recovering the vapours to produce a liquid pitch product;
- iv) processing the liquid product using distillation/evaporation to produce the NR.

The present invention embraces the above method, wherein the step of processing uses the liquid product obtained from a primary recovery unit, a secondary recovery unit, or a combination thereof.

5           This invention also pertains to the above method wherein the step of processing comprises the addition of water to the NR to produce an NR with reduced viscosity.

          This invention relates to the above method wherein the step of processing comprises removing essentially all of the water content of the NR to produce a solid NR.

10           Furthermore, the present invention relates to the method as defined above wherein the step of processing comprises pretreating the liquid product prior to distillation/evaporation. Preferably, the step of pretreating comprises a water wash to reduce viscosity, improve flowability into downstream equipment and enhance the removal of non-resin components.

15           This invention is also directed to a natural resin (NR) characterized by comprising a water content up to about 20%, pH of about 2.0 to about 5.0, and acids content from about 0.1 to about 5 (dry wt%) and a viscosity of about 6 to about 130 cST (@70°C) for liquid NR, or the NR may be solid NR.

20           This invention is also directed to a resin composition that comprises the NR as defined above. Furthermore, this invention is directed to a resin composition comprising NR from about 1% to about 40% (w/w) of the resin composition.

25           This invention is also directed to a resin composition as defined above comprising a phenol-containing or urea containing formaldehyde resin. Furthermore, this invention relates to a resin composition as defined above wherein the phenol-containing or urea-containing formaldehyde resin is selected from the group consisting of phenol formaldehyde, urea formaldehyde, phenol melamine urea formaldehyde, melamine urea formaldehyde, and phenol urea formaldehyde.

30           This invention also relates to a resin composition as defined above wherein the NR comprises from about 20 to about 40% (w/w) of the resin composition. Furthermore, the resin composition of this invention may further be characterized in that a portion of the formaldehyde, within the formaldehyde-phenol resin is replaced with NR, and



wherein the NR replaces up to about 50% of the formaldehyde content of the resin. Preferably the adhesive composition comprises a formaldehyde:phenol ratio from about 1.2:1 to about 3:1. This invention is also directed to a resin composition wherein a portion of the phenol within a formaldehyde phenol resin is replaced with NR.

5

This invention also relates to mixtures of natural resin, comprising whole-oil and fractions of whole-oil. Furthermore, this invention is directed to adhesive compositions and industrial resins comprising natural resin mixtures. This invention also includes phenol-containing formaldehyde resins comprising natural resin, or natural resin mixtures that replaces up to 100% of the phenol content of the phenol-containing resin.

10

This invention also embraces a wood product prepared using the adhesive compositions as defined above. Preferably, the wood product is selected from the group consisting of laminated wood, plywood, particle board, high density particle board, oriented strand board, medium density fiber board, hardboard or wafer board. Furthermore, the wood product prepared using the adhesive composition of this invention is used for exterior, interior or both interior and exterior applications.

15

This invention also pertains to industrial phenol formaldehyde resin products including mouldings, linings, insulation, foundry materials, brake linings, grit binders, for example to be used within abrasives such as sand paper, and the like.

20

Use of a fast pyrolysis process to produce the bio-oil is beneficial in that the fast pyrolysis process depolymerizes and homogenizes the natural glue component of wood, that being lignin, while at the same time other constituents are also depolymerized including cellulose and hemicellulose. The beneficial components are enhanced within NR following the step of distillation/evaporation. The yield of NR, depending upon the biomass feedstock and the fraction of bio-oil used for NR preparation via distillation/evaporation, varies from 15-60% of the feedstock and exhibits properties that are useful within, for example, phenol-containing, or urea-containing formaldehyde resin compositions. The natural resin so produced can be substituted for some of the phenol and formaldehyde, content within phenol-containing formaldehyde resins, and such formulations meet or exceed current phenol formaldehyde resin industry specifications. Furthermore, NR can substitute for some of the formaldehyde within urea-containing

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formaldehyde resins. With removal of the organic acids, the NR can completely substitute for the phenol content in phenol resins, and can also be used within urea-containing formaldehyde resin formulations.

- 5           This summary of the invention does not necessarily describe all necessary features of the invention but that the invention may also reside in a sub-combination of the described features.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

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These and other features of the invention will become more apparent from the following description in which reference is made to the appended drawings wherein:

- 15           **FIGURE 1** shows a schematic of a rapid destructive distillation system, for example, which is not to be considered limiting in any manner, fast pyrolysis.

- 20           **FIGURE 2** shows an aspect of an embodiment of the present invention comprising a flow chart outlining the production of several natural resins. Figure 2 (A) is a schematic showing one of several possible methods for the production of NR60D-WH. Figure 2 (B) shows one of several schematics for the production of NR80D-WH. 1°C and 2°C refer to the liquid products obtained from the primary and secondary recovery unit, respectively.

- 25           **FIGURE 3** shows an aspect of an embodiment of the present invention comprising a flow chart outlining the production of several natural resins. The schematic outlines the one of the possible methods for the production of MNRP-1H and NR60D-2H. 1°C and 2°C refer to the liquid products obtained from the primary and secondary recovery unit, respectively.

- 30           **FIGURE 4** shows an aspect of an embodiment of the present invention comprising a flow chart outlining the production of several natural resins. The schematic outlines the one of the possible methods for the production of NR60D-1H and NR60D-2H. 1°C and 2°C refer to the liquid products obtained from the primary and secondary recovery unit, respectively.

**FIGURE 5** shows an aspect of an embodiment of the present invention comprising a flow chart outlining the production of several natural resins. The schematic outlines the one of the possible methods for the production of NR60D-1H, NR60D-2H, and NR60D-WH. 1°C and 2°C refer to the liquid products obtained from the primary and secondary recovery unit, respectively.

## DESCRIPTION OF PREFERRED EMBODIMENT

The present invention relates to the production and use of a natural resin, a highly reactive ligninic product, derived from wood bark and other biomass residues using rapid destructive distillation, for example, fast pyrolysis.

The following description is of a preferred embodiment by way of example only and without limitation to the combination of features necessary for carrying the invention into effect.

By "bio-oil", "whole-oil" or "light pitch" it is meant the whole liquid fraction obtained following rapid destructive distillation, for example fast pyrolysis, of wood or other biomass, including for example, softwood, hardwood, bark, or agricultural residues. Fast pyrolysis can be achieved by rapid heat transfer to the feed material, by rapid removal of the product via a vacuum, or by a combination of rapid heat transfer and pyrolysis under vacuum. The whole oil is obtained from the product vapour which is produced along with char following pyrolysis. Upon removal of the char the product vapour is condensed and collected within one or more recovery units, for example one or more condensers which may be linked in series. Whole-oil, bio-oil or light pitch refers to the combination of the condensed products obtained from all of the recovery units. Whole oil, or a fraction of the whole-oil which can obtained from at least one of the recovery units as described below, or a combination of whole oil and a selected product fraction, or a combination of different selected product fractions, may be used as a feedstock for further processing according to the methods of the present invention in order to produce a natural resin. By "oil feedstock", it is meant a whole-oil or light-pitch, or a selected product fraction of the whole oil or light pitch, or a combination thereof, that may be used for further processing as described herein.

By "selected product fraction", or "fraction of the whole oil" it is meant a fraction of the liquid product that is obtained from a product vapour following removal of char and condensation. For example, which is not to be considered limiting in any manner, the selected product fraction may comprise the liquid product obtained from at least one  
5 recovery unit, for example a primary recovery unit, a secondary recovery unit, or a combination thereof. The selected product fraction may be used as a feedstock for further processing in order to produce an NR of the present invention, or it may be combined with a whole-oil or another selected product fraction to produce an NR.

10 By "recovery unit" it is meant a device that collects product vapours produced during pyrolysis. A recovery unit may include, but is not limited to, a condenser means which cools and collects a liquid product from the product vapour as is known within the art. A recovery unit may also include de-misters, fiber filter beds or other devices used within the art to collect the liquid product from the product vapour. A recovery unit may  
15 comprise one or more components, for example, one or more condensers, which are typically linked in series.

By "distillation/evaporation" it is meant the processing of a whole-oil or light pitch, or a selected product fraction, via non-destructive techniques in order to drive off  
20 water, acids, for example, but not limited to acetic acid, odorous and non-resin components or a combination thereof. The product of this step may be used as an NR, or it may be further processed, for example but not limited to, the addition of water, in order to produce an NR. The step of distillation/evaporation provides for a controlled polymerization of the feedstock and maintains reactive lignin sites in the product.  
25 Typically, the non-destructive techniques for distillation/evaporation include, but are not limited to:

- evaporation, for example wipe film evaporation (W.F.E), roto-evaporation, agitated film evaporation, short tube vertical evaporation long tube horizontal evaporation, or other evaporation techniques known within the art;
- 30 • distillation, for example, but not limited to vacuum distillation;
- heat exchange, for example, but not limited to, falling film exchanger, scraped surface exchanger, or Teflon® heat exchanger;

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- water treatment, for example, but not limited to the addition of water, or a water-base solution comprising for example NaOH or KOH, at a temperature of from about 40°C to about 60°C;

or other physical or chemical process which removes, evaporates, isolates or otherwise drives off acids, volatiles, water and other light components which are less effective in terms of resin properties and which contain odorous components. Such techniques are known to one of skill in the art, see for example Perry's Chemical Engineers Handbook (6th Edition, R.H. Perry and D. Green eds, 1984; which is incorporated by reference).

Processing of the feedstock by distillation/evaporation can be controlled to produce an optimized degree of cross-linking or polymerization. Without intending to limit the present invention in any manner, NR can be prepared by heating the oil feedstock under vacuum to a temperature which is sufficient to devolatilize odorous and non-resin components. If a liquid NR is to be produced, the water content of the oil feedstock may be monitored during distillation/evaporation to determine the degree of devolatilization so that a final water content of the intermediate liquid NR product is between about 1 and about 10 wt% is obtained. Preferably the final water content of the intermediate liquid NR product is between about 1 and about 5 wt%. The moisture content of the intermediate NR product is further adjusted to produce the final liquid NR product. For solid NR the water content is from about 1 to about 8 wt%, however, this NR is in a more polymerized state. The degree of polymerization may be controlled by the amount of heat used during distillation/evaporation, the amount of time the whole-oil or fraction thereof is subjected to the heat, or a combination thereof. Typically, the more heat or the longer the feedstock is subjected to the heat, or both more heat and longer exposure to heat, results in a more viscous product with a higher average molecular weight than the feedstock. Furthermore, it has been observed that the step of distillation/evaporation increases the proportion of phenolic-enhancer components within the NR.

The natural resin (NR) of this invention may comprise a whole-oil product that has undergone a controlled polymerization through distillation/evaporation, or it may include a selected product fraction of the whole liquid product that has been processed through distillation/evaporation, or it may include a combination of the whole-oil and selected product fraction that has been subjected to distillation/evaporation. NR includes

both a liquid NR, for example NR60, as well as a solid NR, for example MNRP. Liquid NR's may span a range of viscosities and comprising a range of phenolic contents as described herein. Furthermore, the oil feedstock may be pretreated prior to the step of distillation/evaporation, and it may be further processed following  
5 distillation/evaporation.

The oil feedstock is preferably produced from the destructive distillation of wood, using for example, but not limited to fast pyrolysis. However, other processes that are able to liquefy wood may also be used to prepare an oil feedstock from which a NR may  
10 be obtained. Fast pyrolysis can be achieved by rapid heat transfer to the feed material, by rapid removal of the product via a vacuum, or by a combination of rapid heat transfer and pyrolysis under vacuum. The oil feedstock obtained from fast pyrolysis is primarily comprised of depolymerized lignin and other reactive components including phenolics which provide an array of active sites for binding and cross linking within the NR  
15 formulations of the present invention. Non-reactive components are removed during the preparation of the NR, including the distillation/evaporation of the whole-oil, selected product fraction, or a combination thereof, or other steps for pretreating the oil feedstock, for example water washing (see below), prior to processing using distillation/evaporation. The isolated NR fraction is not typically subject to solvent or other fractionation  
20 processes used in the prior art, nor is it condensed (i.e. subject to condensation reactions) as would be typically done for conventional, or vacuum pyrolysis liquid products. Without wishing to be bound by theory, it is possible that the omission of such condensation reactions during the production of the NR of this invention is a primary reason for the high reactivity of NR as a resin agent. However, it is to be understood that  
25 the production of NR, described herein, may include one or more solvent extraction, or other concentration or purification steps as required.

By "MNRP" it is meant an NR that has had the acids, water and other non-reactive components removed via distillation/evaporation, or an other analogous process,  
30 to produce a solid NR product. MNRP may be ground, comminuted, and sized to a desired specification prior to use.

The NR of the present invention may be in the form of a liquid product, comprising activated lignin and spanning a range of viscosities from about 6 to about 130

cSt (@70°C), for example, but not limited to NR60 (e.g. NR60D-1H, NR60D-2H, NR60D-WH), and NR80 (e.g. NR80D-1H, NR80D-2H, NR80D-WH), or it may be a solid NR lignin product, for example, but not limited to MNRP (e.g. MNRP-1H(70), MNRP-2H(70), MNRP-WH(70)) or "V-additive lignin". Various viscosities of NR may also be produced depending upon the temperature, duration and type of distillation/evaporation process used to produce NR. Liquid NR is characterized as being more polymerized, having a higher viscosity and a higher average molecular weight than the oil feedstock. Examples of schematics outlining the preparation of several NR's of the present invention are provided in Figures 2-5. With reference to these figures, it can readily be seen that various combinations and permutations for processing the various oil feedstocks and NR's produced from these feedstocks, may take place. Therefore, it is to be understood that the methods outlined in these figures are examples of several methods for producing NR, and are not to be considered limiting in any manner, as other NR's may be obtained by methods not disclosed within these figures.

15

NR is typically characterized by comprising a water content from about 2 to about 20%, pH of about 2.0 to about 5.0, and acids content from about 0.1 to about 5 (dry wt%) and a viscosity of about 6 to about 130 cSt (@70°C) for liquid NR, as in the case for example, but not limited to NR-60D, or the NR may be a solid NR as in the case of MNRP. Furthermore, NR is characterized as having an increased concentration of phenolics and enhancers, as indicated by its NRP Index from about 50 to about 100, over that of light pitch (whole-oil), having an NRP Index of about 23 to about 30 (see Tables 3a and 3b, Example 2). NR is also characterized as having a higher average molecular weight (AMW), when compared to light-pitch. For example, NR-60D-WH has a wet AMW of about 306, and a dry AMW of about 363, while light-pitch is characterized as having a wet AMV of about 232 and a dry AMW of about 299. MNRP has an even higher AMV of about 388 (wet) and about 412 (dry). The total phenolic content of NR, for example, but not limited to NR60D-2H is from about 40 to about 45 %wt, and greater than that of whole-oil, from about 30%wt to about 35 %wt (See Table 3c, Example 2). The total phenolic content of MNRP is greater than that of NR60D-2H.

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A highly polymerized NR, called V-additive lignin is further characterized as having a high phenolic content of about 95%, a water content of about 3%, and a melting point from about 110°C to about 150°C (see Table 3d Example 2). This NR is a

thermoplastic product and is suitable for use within industrial applications, for example as a plasticizer that can be used within foundry resin formulations as a binder for cores or admixed with moulding sand or clays, as an asphalt emulsifier, or as a concrete additive to increase the aeration quality of concrete.

5

NR is more reactive, and comprises less acid and other odorous components than the oil feedstock. The removal of acids ensures the maintenance of optimal resin properties upon rehydration, if required, and during the use of NR as an adhesive. Furthermore, a lower content of acids requires less addition of caustic during adhesive  
10 formulation which otherwise weakens the wet property of the adhesive. V-additive lignin also has properties that make it suitable for a range of different industrial applications for example as a foundry resin, concrete additive, or asphalt emulsifier. NR obtained following distillation/evaporation comprises a complex mixture of enhancer compounds, for example, but not limited to, aldehydes and ketones, and active phenolic compounds  
15 comprised of monomers and oligomers. NR therefore has the ability to co-react with, or be used as a substitute for, phenol within phenol/formaldehyde (PF) resins.

By "phenolics" or "ligninic" it is meant phenolic polymers which retain the essential characteristics of their natural precursors (natural lignin is a phenolic polymer  
20 which holds wood and bark fibres together and which gives wood its strength), but are activated for use in resin formulations, or as additives in other industrial applications.

By "enhancers" it is meant carbonyl compounds, typically light aldehydes and ketones.

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The NR-containing resins of the present invention may be used in the same manner as phenol-formaldehyde resins are typically used. For example, which is not to be considered limiting in any manner, resins compositions comprising NR may be used to produce industrial phenol formaldehyde resin products including mouldings, linings,  
30 insulation, foundry materials, brake linings, grit binders, for example, those used with abrasives such as sand paper, and the like. Furthermore, NR comprising resins may be used as adhesives for the product of wood products and the like.



Fast pyrolysis of wood or other biomass residues results in the preparation of product vapours and char. After removal of the char components from the product stream, the product vapours are condensed to obtain a whole-oil, or bio-oil product from pyrolysis. A suitable fast pyrolysis process for preparing such a bio-oil is described in  
5 WO 91/11499 (Freel and Graham, published August 8, 1991, which is incorporated by reference), and is diagrammatically presented in Figure 1. Briefly, the system includes a feed system (10), a reactor (20), a particulate inorganic heat carrier reheating system (30), and for the purposes of the invention described herein, at least one recovery unit, which as shown in Figure 1, and which is not to be considered limiting in any manner,  
10 may comprise a primary (40) and a secondary (50) condenser through which the product vapours produced during pyrolysis are cooled and collected using a suitable condenser means (80). The recovery unit may also include, a de-mister (60) and a fiber filter bed (70) or other device to collect the liquid product. The NR of this invention may be derived from a selected product fraction obtained from at least one recovery unit, for  
15 example the primary, or the secondary recovery unit, or a combination thereof, or it may be a whole-oil, obtained from first and second recovery units, including de-misters and fiber filter bed, or a combination thereof. However, it is to be understood that analogous fast pyrolysis systems, comprising different number or size of recovery units, or different condensing means may be used for the selective preparation of the oil feedstock for the  
20 purpose of the present invention.

The recovery unit system used within the fast pyrolysis reactor system, outlined in Figure 1, which is not to be considered limiting in any manner, involves the use of direct-liquid contact condensers (80) to cool the pyrolytic oil product. However, it is to  
25 be understood that any suitable recovery unit may be used. In the preferred embodiment, liquid, used within these condensers (80) to cool the pyrolytic product, is obtained from the corresponding cooled primary or secondary condenser product (90; Figure 1). However, as would be evident to one of skill in the art, any other compatible liquid for cooling the product within the primary and secondary recovery units, or a combination  
30 thereof, may also be used for this purpose. Furthermore, it is considered within the scope of this invention that other scrubber or cooling means including heat exchanges comprising solid surfaces and the like may also be used for cooling the product vapours. Bio-oils of the prior art may be processed using the methods of the present invention to produce a NR suitable for use within adhesive formulations.

Suitable oil feedstocks for the purposes of the present invention may be produced using the method and apparatus disclosed in WO 91/11499 (which is incorporated by reference). These oil feedstocks are typically characterized by the properties outlined in Example 1, however, it is to be understood that the properties defined in Example 1 vary  
5 depending upon the lignocellulosic feedstock used for fast pyrolysis. Other oil feedstocks, comprising different properties than those listed in Example 1 may be used for the methods as described herein.

An example, which is not to be considered limiting in any manner, of conditions  
10 of distillation/evaporation for producing a liquid NR obtained from whole-oil, a selected product fraction, or a combination thereof, comprises processing the oil feedstock at about 60°C to about 200°C for about 1 to about 3 hours via roto-evaporation. Preferably, the oil feedstock is maintained at about 110°C to about 130°C for about 1 to about 1.5 hours during this processing step. Similar temperature ranges may be used to prepare  
15 a liquid NR using W.F.E., however, the duration of time where the oil feedstock is present within the W.F.E. apparatus is much shorter (i.e. the transport time through the apparatus), and the oil feedstock can be processed in a continuous and rapid manner. Typically following the distillation/evaporation step, and while the NR is still at about 60°C to about 110°C, water may be added to the NR to reduce the viscosity to the  
20 desired specification. The final liquid NR product so produced is characterized with a viscosity ranging from about 6.0 to about 130 (cSt @ 70°C), and comprises a water content level of from about 10 to about 25 wt%, preferably, the water content is from about 15 to about 18%. One example of a liquid NR produced using roto-evaporation, is NR60D-2H, which when subjected to roto-evaporation for 1 hour at 120°C and  
25 rehydrated, is characterized as having a viscosity of about 70 cSt.(@ 70°C), a pH of about 2.6 and a low acid content of about 2.4 (Dry wt%). However, it is to be understood that by varying the oil feedstock and distillation/evaporation processing parameters a variety of liquid NR's may be produced.

30 An example, which is not to be considered limiting in any manner, of conditions of distillation/evaporation for producing an MNRP (solid NR) obtained from whole-oil, a selected product fraction, or a combination thereof, comprises processing the oil feedstock to roto-evaporation at about 125°C to about 220°C for about 1 to about 3 hours. Preferably, the oil feedstock is maintained at about 160°C to about 200°C for

about 1 to about 1.5 hours. Temperature ranges of from about 90°C to about 160°C may be used with W.F.E in order to process oil feedstock in a batch or continuous manner. An example of a solid NR produced in this manner, is MNRP-1H(70), which may be produced by roto-evaporation for 1 hour at 180°C. Typically, after cooling, the MNRP  
5 is ground and sized to produce a powder as a final product. A variety of solid NR products may be prepared by varying the feedstock, and processing parameters, including V-additive lignin.

The viscosity and degree of polymerization of liquid NR may also be varied by  
10 pretreating a selected product fraction, prior to the step of distillation/evaporation. For example, which is not to be considered limiting, an NR with increased viscosity and degree of polymerization over that of the oil feedstock may be obtained by subjecting a selected product fraction obtained from the first recovery unit to a water wash, prior to distillation/evaporation, or prior to mixing it with a selected product fraction obtained  
15 from the second recovery unit and then proceeding with the step of distillation/evaporation as outlined above. Typically, water at about 30°C to about 80°C, preferably from about 40°C to about 60°C, is added to the oil and mixed together, and the ligninic NR liquid is allowed to concentrate. The non-ligninic liquid comprises acids and other water-soluble components that reduce the reactivity of the final liquid or solid  
20 NR product. Separation and recovery of the non-ligninic liquid concentrates the ligninic oil product. Furthermore, the addition of water to the oil feedstock prior to distillation/evaporation helps in the transfer of the oil feedstock during processing. Water addition also helps to prevent the overcooking of the oil during distillation/evaporation, and it may help enhance the removal of non-resin components from the oil during  
25 distillation/evaporation by providing a carrier for such components. An example, which is not to be considered limiting in any manner, of a washed oil feedstock that is then processed by distillation/evaporation is NR80D-2H.

Therefore the final characteristics of NR may span a range of viscosities and  
30 degrees of polymerization as determined by:

- varying the temperature and treatment time during distillation/evaporation;
- the type of lignocellulosic feedstock used to produce the oil feedstock, for example but not limited to oil feedstock produced by fast pyrolysis;

- the oil feedstock itself, whether it is a whole-oil, or a selected product fraction, or a combination thereof;
- the pretreatment of the oil feedstock; and
- the amount of water added back to liquid NR.

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Therefore, the present invention provides for a range of NR's, with a range of properties, including the degree of cross-linking, polymerization, enhancers, and active phenolic compounds, that may be used as replacements of constituents within adhesive resins, such as phenol formaldehyde, urea formaldehyde, or related resins, or as an asphalt emulsifier, concrete additive, foundry binder, as defined above.

By "phenol-containing formaldehyde resin" it is meant resin compositions that comprises phenol as one of its ingredients. Such resins include but are not limited to phenol formaldehyde (PF), phenolic melamine urea formaldehyde (PMUF), and phenol urea formaldehyde (PUF) resins. Similarly, by "urea-containing formaldehyde resins" it is meant adhesive compositions comprising urea as one of its ingredients, for example, but not limited to, urea formaldehyde (UF), phenol urea formaldehyde (PUF), phenol melamine urea formaldehyde (PMUF), and melamine urea formaldehyde (MUF) resins. Without wishing to be bound by theory, it is thought that the addition of NR (in either solid or liquid form) to urea-containing resins adds or complements the phenol content of these resins due to the high phenolic content of NR. Therefore, a UF resin that is partially replaced with NR may be considered a PUF-like resin.

Without wishing to be bound by theory, it is thought that the processing of the oil-feedstock using distillation/evaporation removes compounds that interfere with the use of bio-oils, for example those found within the prior art, within adhesive resin formulations. Furthermore, the distillation/evaporation process has been found to actually increase the ligninic and enhancer properties within the final NR product, over that found within the oil feedstock. As a result NR is comprised of a predominantly phenolic fraction, containing aldehydes, which provide NR with its desirable properties for use within adhesive formulations. In part this quality of NR is indicated by its NRP (Natural Resin Pure) Index. For example, whole oil has an NRP Index of about 29, NR-60D has an NRP Index of about 60, and MNRP is characterized with an NRP Index of about 90.

The oil feedstock of this invention may also be pretreated to reduce the organic acid content of the resin prior to distillation/evaporation. Any suitable method may be employed for this process, for example, and not wishing to be limited to this method, the feedstock may be washed in water by mixing the feedstock in water, allowing phase separation to take place, and recovering the oil fraction. For example, which is not to be considered limiting in any manner, the oil feedstock is washed in water from about 30°C to about 80°C and left to precipitate. Preferably, the water temperature is from about 40°C to about 60°C. The pretreated feedstock prepared in this manner, comprises the phenolic and aldehyde content of the feedstock, with a dramatically reduced organic acid content when compared with the initial feedstock, and is a more concentrate form of feedstock, containing up to about 80% (w/w) phenolics. This pretreated feedstock may be used for the preparation of NR or MNRP as described herein, for example, but not limited to NR80D-2H.

The NR, or MNRP produced by the method described herein have been substituted for some of the phenol content within PF resins, and such formulations meet or exceed current PF resin industry specifications. NR has been substituted from about 60% to about 100% of the phenol content within PF resins. Resins so produced may comprise up to about 40% (w/w) of NR. Similarly, NR may also be used as replacement within PMUF and, PUF resins. Furthermore, the NR of this invention has successfully replaced up to about 60% (w/w) of the urea formaldehyde within UF resins, and has been effectively used within PMUF and MUF resins. MNRP resins with even higher melting point temperatures, for example above 110°C may also be prepared using the methods as described herein. These high melting point resins are referred to as V-additive lignins and has use within the automotive industry, or as a foundry resin, asphalt emulsifier, or as a concrete additive (see Table 3d, Example 2).

As a result of processing the NR using distillation/evaporation, the recovery technique is more selective than solvent extraction-based methods. For example, the P/N fraction extracted using ethyl acetate (e.g. US 4,942,269; US 5,235,021), results in a fraction comprising a compound that is soluble in this solvent and that is co-extracted along with the desired-for resin compounds. Several of these co-extracted compounds are odorous (e.g. lactone, an acrid compound) while others dilute the P/N resin. The distillation/evaporation technique of this invention is selective in that essentially all of

the desirable resin components (natural phenolics derived from lignin) are recovered, while other non-desired compounds are removed within other fractions. Furthermore, the process of distillation/evaporation has been found to increase the phenolic and enhancer components within NR, when compared to the oil feedstock. As a result, the NR of this invention exhibits many beneficial properties over prior art pyrolytic oil extractions and requires significantly less preparation. For example:

1. NR and MNRP have a slight pleasant "smoky" odour, lacking the acrid smell of solvent extracted fractions. When used within adhesive applications and industrial resin applications, there is no residual odour;
2. in solvent extracted processes, including the process used to obtain P/N, the solvent reacts with residuals in the fraction that is not used for P/N, to form salts. These salts must be recovered using a recovery boiler requiring additional costs, and the residual bio-oil is not available for other commercial applications. NR or MNRP products, on the other hand, are not contaminated with salts as no solvents are used;
3. the processing of oil feedstock by distillation/evaporation is readily accomplished using simple devices and does not require any specialized facilities for handling solvents and the like;
4. the fast pyrolysis method used for the preparation of bio-oil, including NR, has been successfully scaled up from bench-top trials to industrial/commercial production levels (see WO91/11499). Therefore, NR preparations are easily produced on a commercial scale.

#### Characteristics of NR

The NR produced by the method of this invention has been found to be consistent between batch to batch productions runs of NR (as tested when used for OSB production, see below), even when different hardwoods and softwoods are processed by fast pyrolysis.

The free phenol content of a resin formulations is also used to determine the suitability of alternative materials in PF resin formulations. The NR produced following the method of this invention is characterised in having a very low free phenol content, from about 0.001 to about 0.05% (w/w), yet the total phenolic content is quite high, from about 30% to about 80% (w/w) within NR. It is the phenolic content which is very reactive and provides an array of active sites for binding and cross linking within NR formulations.

NR refers to a range of products that are prepared according to the methods of the present invention. Several examples of such products include, but are not limited to:

- NR60D-WH
- NR60D-1H
- NR60D-2H
- NR80D-2H
- MNRP-1H(70)
- MNRP-2H(70)
- V-additive lignin.

Also see Figures 2-5.

20

The above nomenclature is to be interpreted as follows: NR60D-WH, is a liquid NR with an Natural Resin Pure Index (NRP) of 60. The NRP index is a measure of the phenolic and enhancer content of the NR. A higher NRP index indicates a greater proportion of phenolics and enhancers. The "D" associated with NR60, indicates that the NR has been processed by distillation/evaporation (MNRP due to its nature has been processed using distillation/evaporation, and therefore lacks the "D" designation). The oil feedstock for the preparation of the NR may be a whole-oil obtained from a range of lignocellulosic feedstocks, for example hardwood, and "WH" designates such a oil feedstock. The 1H or 2H designation indicates that the oil feedstock is obtained from the primary or secondary recovery unit, respectively, using a hardwood lignocellulosic feedstock (other lignocellulosic feedstocks may also be used). MNRP indicates that the NR is solid. The 1H or 2H designation is the same as above, while "(70)" indicates that the melting point of the MNRP is 70°C. V-additive lignin is a highly polymerized MNRP characterized in that it has a melting point above 110°C.

Several of these NR's are characterized by the parameters listed in Example 2 however, it is to be understood that other NR may be produced with properties that differ from those listed in Example 2.

5           The final NR product of this invention comprises up to about 20% water, however, NR is insoluble in water due to its low polarity and high content of non-polar organics. By increasing the pH of the NR (to about 10) and converting it into its phenoxide ion form it obtains a gum-like consistency, is water soluble and can be used within formaldehyde-phenol formulations. MNRP is not soluble in water and is used in  
10 its powdered form within adhesive formulations. NR, both solid and liquid, is soluble in polar organic solvents for example acetone, methanol, ethanol and isopropanol. Due to the hydrophobicity of NR, it is chemically compatible in the formulation of phenolic-based resins. Liquid NR is soluble in a mixture of water/phenol, and when reacted with formaldehyde, gives methanol-water soluble derivatives. Liquid NR (for example NR60)  
15 and solid NR (for example MNRP) are both soluble in the basic formulation of a P/F

When compared with whole-oil, NR is typically characterized by comprising a lower water and acid content, a higher viscosity, NRP Index and average molecular weight than whole oil. For example, which is not to be considered limiting in any  
20 manner, a comparison of NR60D-2H with whole-oil indicates that NR60D-2H comprises:

- a lower water content (from about 5 to about 20 wt%), than that of whole-oil (about 23-30 wt%);
- 25 • a lower acid content of about 0.1 to about 5 dry wt%, compared with an acid content of about 7 to about 12 dry wt% of whole oil;
- a viscosity of about 20 to about 130 cST (@70°C), compared with a viscosity of whole oil of about 5 to about 10 cST (@70°C);
- an increased concentration of phenolics and enhancers (NRP Index from about  
30 50 to about 100), compared with whole-oil having an NRP Index of about 23 to about 30;
- a higher average molecular weight (wet - about 306; dry about 363) compared to whole oil (wet - about 232; dry about 299); and



- a total phenolic content from about 40 wt% to about 45 wt%, compared with that of whole-oil, from about 30 wt% to about 35 wt%.

A highly polymerized NR with a high melting point typically about 110°C is called V-additive lignin. This NR is produced by increasing the time, temperature, or both time and temperature during distillation/evaporation. V-additive lignin is characterized as having a high phenolic content of about 95%, a water content of about 3%, a melting point from about 110°C to about 150°C, a flash point greater than 280°C, and a density of about 1.25 g/cm<sup>3</sup> (see Table 3d Example 2). V-additive lignin may be commuted to a powder or produced in a flake-like form prior to use. This NR is a thermoplastic product and is suitable for use within industrial applications, for example as a plasticizer that can be used within foundry resin formulations and admixed with sand, as an asphalt emulsifier, or as a concrete additive to increase the aeration quality of concrete. V-additive lignin may also be used within the automotive industry.

15

Calometric analysis indicates that NR has a net caloric value of about 4355 cal/g (18.22 MJ/kg), with a gross caloric value of about 4690 cal/g (19.62 MJ/kg).

NR may be obtained from a variety of lignocellulosic feedstock sources including softwood, hardwood, bark, white wood, or other lignocellulosic biomass feedstocks, for example, bagasse (sugar cane residue).

20

#### **NR-containing Phenol Formaldehyde (PF), or Urea Formaldehyde (UF) Resins**

In order to formulate NR within phenol-containing formaldehyde, or urea-containing formaldehyde resins, phenol or urea, water, paraformaldehyde, and other ingredients of the adhesive are mixed together and heated if required to dissolve the ingredients. If heated, the mixture is cooled prior to the addition of NR. Caustic (for example NaOH) is added to the mixture containing phenol or urea, formaldehyde and NR, to a desired pH. The addition of caustic ensures the solubilization of the NR, and initiates the reaction. This mixture may then be heated or cooled, and more caustic added during the preparation of the resin, as required. The resin is typically maintained at 10°C until use, and exhibits similar stability associated with commercial PF resin formulations.

25

30

Phenolic melamine urea formaldehyde (PMUF), melamine urea formaldehyde (MUF), phenol urea formaldehyde (PUF) resins are prepared in a similar manner.

NR can be added up to about 60% to about 100% (w/w) of the phenol content of the resin. Furthermore, the formaldehyde content of phenol-containing or urea-containing resins may be substituted with NR due to the natural aldehydes present within NR, for example NR can be used to replace up to about 50% (w/w) of the formaldehyde content of these resins. Similarly, up to about 60% (w/w) of the urea-formaldehyde content of a UF resin may be replaced using NR. Therefore, PF, UF and related resins may be formulated that contain up to about 40% (w/w) NR of the total resin composition. As disclosed in Example 3, NR produced as described herein is suitable for use as a phenol substitute within PF resins. However, this is not the case for Whole-oil (light pitch), which when used within PF resins as a substitute for 40% phenol, produced inferior OSB and waferboard panels (see Example 3, Table 5) that did not meet CSA Standard 0437.093.

Resins prepared using NR may be used for a variety of purposes including, but not limited to, the preparation of wood products, for example, laminated wood, plywood, particle board, high density particle board, oriented strand board, medium density fibre board, hardboard, or wafer board. Furthermore, NR-containing resins may also be used for the manufacture of industrial phenol formaldehyde resin products, for example, but not limited to, mouldings, linings, insulation, as foundry resins, asphalt emulsifiers, concrete additives, for brake linings, as grit binders and the like.

## **25 Board manufacture using NR-containing resins**

The phenol-containing or urea-containing formaldehyde resins prepared above may be used for the production of a range of board products, for example, but not limited to, laminate wood boards, plywood, particle board, high density particle board, oriented strand board, medium density fiber board, hardboard, or wafer board. NR-containing PF resins are used within boards to be subject to exterior use due to the excellent water repellency of the resin. Typically UF resins are not desired for outside use, however, NR-containing UF resins may have application for exterior use due to the reduced

swelling observed in boards prepared with urea formaldehyde adhesives comprising NR, compared with boards prepared using commercial UF resin.

5 NR containing PF or UF resins can be used for the production of oriented strand board (OSB) as outlined below. However, it is to be understood that this application of NR-containing resin is not to be considered limiting in any manner, as other wood derived products prepared using commercially available PF, UF, or related resins, which are commonly known within the art, may be prepared using resin formulations comprising NR.

10

Oriented strand boards may prepared using standards methods that are known to those of skill in the art. For example, but not to be considered limiting in any manner, the production of OSB may involve the following parameters:

- 15 wood matrix: particulate wood product, wood chips, wafers, veneer or plywood etc.
- Panel thickness: from about 1/16" to 2"
- Resin content: from about 0.5 to about 20.0%
- Wax content: from about 0.5 to about 5%
- 20 Mat moisture: from about 2 to about 10%
- Press time: from about 2 min to 30 min
- Press temperature: from about 150 °C to about 275 °C

25 It is to be understood that these parameters may be adjusted as required in order to produce a suitable board product using NR-containing resins of this invention.

Oriented strand boards, or other board types, as listed above, that are prepared using NR-containing PF resins are readily tested for suitability within the industry. For example, the OSB boards prepared as described herein have been tested according to the Canadian product standard for OSB (CSA 0437.1-93, April 1993). These tests include; 30 determination of density, internal bond (IB), modulus of rupture (MOR), and modulus of elasticity (MOE) and the minimum properties to meet this standard are listed below (Table 1):

Table 1: CSA 0437.103 Standard

Parameter	Grade R-1	Units
Modulus of Rupture (MOR)	17.2	MPa
5 Modulus of Elasticity (MOE)	3100	MPa
MOR after 2-h boil (wet)	8.6	MPa
Internal Bond (IB)	0.345	MPa
Thickness Swell	15	%
10 Water Adsorption	N/A	%

10

Results of these tests indicate that phenol may be replaced by NR from about 10 up to 100 % (w/w), and produce a OSB product that meets industrial standards, and that is equivalent to, or exceeds OSBs prepared using commercially available phenol-containing, or urea-containing formaldehyde resins. Furthermore, OSB boards prepared with NR-containing resins require less formaldehyde within resin formulations for equivalent cross-linking and binding properties as typically found with control resin formulations.

15

Without wishing to be bound by theory, it is thought that the natural carbonyl components (such as aldehydes and ketones) within NR permits the use of less formaldehyde. In applications which require lower strength adhesive, the NR can be used alone without any addition of formaldehyde, but it is preferable to add formaldehyde to obtain a better resin. These carbonyl compounds have a molecular weight from about 30 to about 800 Daltons, and comprise about 23% of the NR

20

25

The NR produced following the method of this invention has a dark brown colour, and when formulated into a resin, results in a dark reddish brown colour. However, during production runs using NR, OSB boards are lighter in colour than PF control boards. Furthermore, the NR has a mild, pleasant odour, yet OSB boards prepared using NR have no resultant odour. The odour can be reduced following heating of the NR, or through the removal of volatiles via flushing. The NR of this invention is

30

also characterized by being acidic (pH ~2.3), however, the acid content of NR is substantially reduced compared with that of the oil feedstock.

5 The above description is not intended to limit the claimed invention in any manner, furthermore, the discussed combination of features might not be absolutely necessary for the inventive solution.

10 The present invention will be further illustrated in the following examples. However it is to be understood that these examples are for illustrative purposes only, and should not be used to limit the scope of the present invention in any manner.

### Examples

#### Example 1: Method for obtaining, and the characteristics of, oil feedstocks

15

Oil feedstock is obtained using red maple feedstock within a fast pyrolysis reactor as described in WO 91/11499 (which is incorporated herein by reference). Red maple feedstock is supplied to the reactor at a feedstock to heat carrier ratio of from about 5:1 to about 200:1. The char is rapidly separated from the product vapour/gas stream, and  
20 the product vapour rapidly quenched within the primary recovery unit using, for example, a direct liquid contact condenser. The compounds remaining within the product vapour are transferred to a secondary recovery unit linked to the primary recovery unit in series. The product vapour is then quenched using, for example a direct-liquid contact condenser within the secondary recovery unit, and the condensed product collected. Any remaining  
25 product within the product vapour is collected within the demister and filter bed (see Figure 1). The primary recovery unit product is collected, as well as the secondary recovery unit product. The yield of product oil, using red maple as a feedstock, from the primary recovery unit ranges from about 40 to about 60% (w/w), and is typically about 53.3%. The yield of oil from the secondary recovery unit ranges from about 12 to about  
30 25 % (w/w) and is typically about 19.7%.

The oil feedstock is characterized as exhibiting a low free phenol content ranging from 0.001 to 0.1% (w/w); total phenolic content from about 10-80% (w/w); a dark brown colour and a mild, pleasant smoky odour; a pH of about 2.0 to about 2.8 (see Table

2); insolubility in water; and solubility in organic solvents including acetone, methanol, ethanol and isopropanol.

**Table 2: Properties of Oil feedstock**

5

Oil feedstock	pH	Water content (wt%)	Acid Content (Dry wt%)	Viscosity (cSt @ 70°C	NRP Index	A.M.W.* Wet/Dry
Primary Recovery unit	2	36	12	3	22	n/d***
Secondary Recovery unit	2	18	8	15	48	n/d
Whole-oil**	2	24	10	6	30	232/299

10

\*Average Molecular Weight

\*\* combination of primary and secondary recovery unit oil-products.

\*\*\* not determined

15

The oil feedstock is optionally washed with 3 volumes water at 50°C, the phases allowed to separate, and the oil-layer retained, to produce a washed oil feedstock that is characterized in having a more neutral pH, and up to 90% less organic acid content when compared with the oil feedstock. Furthermore, the phenolic content of washed oil feedstock is up to about 80% (w/w) or more, due to the removal of the organic acid component, and is a more concentrate form of oil feedstock.

20

## **Example 2: Preparation and analysis of liquid NR, MNRP and V-additive Lignin**

### **Liquid NR production using rotoevaporation**

25

Oil feedstocks from Example 1 are processed by distillation/evaporation at 120°C for 1 hour under vacuum of 26"Hg to a water content of about 3% (wt%) to produce an NR. The product is removed and water is added to the liquid NR when the NR reaches a temperature of about 80°C to make a final water content of 16-18 (wt%). The NR is mixed well and allowed to cool to room temperature.

30

Liquid NR is typically characterized by comprising a water content of from about 10 to about 20 wt%, pH of about 2.0 to about 5.0, an acids content from about 0.1 to about 5 (dry wt%), an average molecular weight (wet)/(dry) of from about (250-350)/(280-380) Daltons, and a viscosity of about 6 to about 130 cST (@70°C). Analysis  
5 of liquid NR is presented in Tables 2 and 3 below.

#### Solid MNRP production using rotoevaporation

Oil feedstocks from Example 1 are processed by distillation/evaporation at 180°C  
10 for 1 hour under vacuum of 26"Hg. The product is decanted while hot, cooled to solidify, and ground to a powder. To produce an MNRP with an 80°C or a 100°C melting point, the oil feedstock is rotoevaporated for 1 hour 10 min, or 1 hour 20 min, respectively.

Solid NR is characterized by comprising a water content of from about 3 to about  
15 10 wt%, pH of about 2.0 to about 5.0, an acids content from about 0.1 to about 5 (dry wt%), an average molecular weight (wet)/(dry) of from about (300-450)/(350-500) Daltons, and is a solid at room temperature.

Examples of the properties of several solid NR's prepared from primary,  
20 secondary recovery units are presented in Table 3. These parameters are typical for each defined sample, however, they are obtained from one sample and variations in these values are to be expected.

Both the liquid and solid NR's are generally characterized as having a lower acid  
25 content, higher pH, higher viscosity, an increased average molecular weight, and a higher concentration of phenolics and enhancers as indicated by the NRP Index, than the oil feedstock (compare Tables 2, above and Table 3, below).

#### Wiped Film Evaporation of NR

30

Oil feedstocks from Example 1 are processed by WFE at 80°C, for liquid NR, or 140°C for MNRP, in a continuous or batch mode under vacuum of 26"Hg. The oil feedstock is added to the WFE at a feed rate within a range of 20 to 50 lbs./hr per square foot of heated surface area. Once liquid is observed flowing through the viewing port on

the resin outlet of the WFE, the rotor is turned on between 130 and 300 revolutions per minute. The liquid is distributed centrifugally to the heated wall and a film is created by the moving wiper blades. All pipes used to transport the NR are heated to 150°C. The concentrated resin is tapped off after an appropriate amount of time.

5

Batch System: Vacuum is isolated with top valve of resin vessel and resin is drained into a container. When all resin has drained, the drain valve is closed and the vacuum is reintroduced to vessel. The concentrated resin is weighed, and for liquid NR, an appropriate amount of water to produce a product with 16% to 18% by weight is added. The product is mixed thoroughly with drill mixer and a sample is taken for analysis. No water is added for MNRP (solid NR).

10

Continuous System: A height for the level setpoint is set and the bleed line control valve is adjusted to the mixing tank to keep this level constant. For liquid NR, the water flow rate setpoint is set to a value that produces a product with a water content of 16% to 18%. A high shear mixer mounted on mixing vessel is used to mix water and resin thoroughly. Periodically take samples for analysis. No water is added for MNRP.

15

NR's produced from primary or secondary recovery units, or whole oil, using WFE exhibit the same properties as those listed in Table 3, below.

20

Yields of NR60D-1H, using red maple as the lignocellulosic feedstock, ranges from about 16 to about 26% (w/w), and typically are about 23% (w/w). Yields of NR60D-2H range from about 12 to about 20% (w/w), and are typically about 17% (w/w). Yields of HR60D-WH range from 32 to about 48 % (w/w) and are typically 40% (w/w).

25

Examples of the properties of several NR's prepared from the secondary recovery unit or whole-oil fraction are presented in Tables 3a and 3b. These parameters are typical for each defined sample, however, they are obtained from one sample and variations in these values are to be expected.

30



Table 3a: Properties of NR

NR	Water content (wt%)	pH	Acid content (Dry wt%)	A.M.W.* Wet/Dry	NRP Index	Melting Point (°C)	Viscosity @ 70°C (cSt)
NR60D-WH	16.5	2.6	2.4	306/363	60	liquid	110
NR60D-2H	16.5	2.6	2.4	287/340	60	liquid	70
MNRP-1H(70)	6	2.5	0.7	n/d**	90	70	solid
MNRP-2H(70)	6	2.5	0.7	388/412	90	70	solid

\*Average Molecular Weight, Daltons

\*\* not determined

Table 3b: Detailed properties of NR-60D-2H compared with Whole Oil

Characteristic	Whole Oil	NR-60D-2H
pH	2.26	2.36
Water Content (wt%)	23.4	17.4
Acid Content (dry wt%)	9.9	2.4
Viscosity @ 70°C (cSt)	8	70
NRP Index	29	61
Ash Content (wt%)	0.08	0.03
AMW (wet/dry)	232/299	287/340
Carbon	44.90	51.22
Hydrogen	7.33	6.89
Nitrogen	0.21	0.29
Sulfur	0.05	0.05
Oxygen	24.03	24.12

A comparison of the phenolics, as determined by GC(TOF)MS within of whole-oil and NR60D-2H is provided in Table 3c. The data in this Table are an extract of the analysis, highlighting most of the phenolics in these samples, and indicate that the total phenolic content (determined from the complete analysis) of whole-oil is about 33.9 wt%, and for NR60D-2H, the total phenolic content is about 42.5 wt%.

**Table 3c: Comparison of phenolic content between whole-oil and NR60D-2H derived from GC(TOF)MS analysis (\* R.T. Retention Time in secs. These are approx. times using whole oil analysis for the reference R.T.. Variations in time exist between analysis. Where times differ between whole oil and NR60D-2H, the R.T. is left blank).**

5

	R.T.*	Name	Whole Oil		NR60D-2H	
			Area%	Peak #	Area%	Peak #
	241.61	Phenol	6.5061	41	4.3904	40
	364.11	Phenol, 2-methyl	1.7123	66	1.5168	69
10	412.11	Phenol, 2-methoxy	2.0703	74	2.2143	79
	452.61	Phenol, 2,3-dimethyl	0.32788	82	0.30263	89
	543.11	Phenol, 2-ethyl	0.40623	93	0.084498	108
	558.12	Ethanone, 1-(2-hydroxyphenol)			0.024522	111
	560.61	Phenol, 2,4-dimethyl	0.25740	95	0.64672	112
15	564.11	Phenol, 2-(2-propenyl)-(Tent) DB5-802	0.024792	96		
	567.61	2,5-Dihydroxybenzaldehyde	0.074999	97	0.27138	114
	608.11	Phenol, 4-ethyl	0.042256	101		
	614.11	Phenol, 2-ethyl	0.033676	104		
	627.61	Phenol, 3,4-dimethyl	0.17496	105		
20	644.61	Phenol, 2-methoxy-4-methyl	1.2882	108	0.36706	119
		Phenol, 3-ethyl			0.037461	120
	665.61	Phenol, 3,4-dimethyl	0.13768	112	0.15799	121
		Phenol, 2-methoxy-4-methyl			1.4152	123
	666.12	Phenol, 3,4-dimethyl			0.15818	128
25	672.11	Phenol, 2,4,6-trimethyl	0.21058	113	0.15089	129
	700.61	1,2-Benzenediol	0.74677	117	0.017686	134
	748.12	Resorcinol Monoacetate			0.26544	138
	752.61	Phenol, 3-(1-methylethyl)-	0.19326	120	0.16743	139
	773.61	Phenol, 3-(1-methylethyl)	0.64036	122	0.64365	141

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	R.T.*	Name	Whole Oil		NR60D-2H	
			Area%	Peak #	Area%	Peak #
		785.11 Phenol, 3-(1-methylethyl)	0.078711	126		
		806.11 1,2-Benzenediol,3-methoxy	0.092985	127	1.3222	144
5		809.11 Phenol, 4-ethyl-2-methoxy-	0.050523	128	0.58397	146
		819.11 Phenol, 2-(2-propenyl), (Tent) DB5-802	0.021504	129		
		836.62 Phenyl, 3,4,5-trimethyl			0.052516	149
		836.61 1,2-Benzenediol, 4-methyl	0.0044058	134	0.93860	150
		853.11 Phenol, 4-ethyl-2-methoxy	0.10123	138	.11244	152
10		889.12 Thymol			0.18315	157
		889.11 Phenol, p-tert-butyl	0.15713	142		
		914.61 1,2-Benzenediol,4-methyl	0.063533	146		
		923.11 Benzene, (3-methyl-2-butenyl)-	0.034630	147		
		935.11 4-Hydroxy-3- methylacetophenone	0.24843	148		
15		949.11 Phenol,2-(1,1-dimethylethyl)-5- methyl-	0.0091629	151		
		956.61 Benzaldehyde,4-hydroxy	0.085893	152		
		1033.1 2-Methoxy-5-methylphenol	0.27300	158		
		917.62 1,2-Benzenediol, 4-methyl			1.5103	160
		960.12 Benzaldehyde, 4-hydroxy			0.37630	165
20		1034.1 Phenol, 2-methoxy-4-methyl			0.31506	173
		1034.6 Phenol, 2,6-dimethoxy	1.3823	159	1.9856	174
		1045.1 Phenol, 2-methoxy-5-(1- propenyl)-,(E)-	0.20728	162	.28363	175
		1057.6 1,4-Benzenediol,2-methyl	0.068245	164	.032946	178
		1060.1 Phenol, 2-methoxy-4-propyl			0.25673	179
25		1092.6 Benzaldehyde, 4-hydroxy	0.075885	167		
		1133.6 Vanillin	0.68202	173	.055973	182

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	R.T.*	Name	Whole Oil		NR60D-2H	
			Area%	Peak #	Area%	Peak #
	1138.1	1,3-Benzenediol, 4-ethyl	0.25115	174		
	1140.1	1,3-Benzenediol, 4-ethyl			0.35844	183
5	1163.1	Phenol, 2-methoxy-4-(1-propenyl)-	0.14949	177	0.19770	186
	1169.1	Ethanone, 1-(2-hydroxyphenyl)-			0.10464	187
	1228.6	1,3-Benzenediol, 4-ethyl	0.071847	190	0.37727	194
	1245.6	4-Nonylphenol	0.018417	194		
	1254.1	Benzoic acid, 4-hydroxy-3-methoxy	0.27811	196		
10	1229.6	Benzeneacetic acid, $\alpha$ , 4-dihydroxy			0.087292	197
	1255.1	Ethanone, 1-(2,3,4-trihydroxyphenyl)			0.21500	199
	1257.1	Phenol, 2-methoxy-5-(1-propenyl)-, (E)-	0.29094	197	0.37792	200
	1272.6	Phenol, 4-ethyl-2-methoxy	0.046344	200	0.062325	202
	1277.6	Ethanone, 1-(2-hydroxyphenyl)			0.12035	203
15	1281.6	Benzaldehyde, 2-hydroxy-, oxime			0.042618	204
	1317.1	Benzeneacetaldehyde, $\alpha$ -phenyl			0.012898	209
	1333.1	3-tert-Butyl-4-hydroxyanisole			1.1684	210
	1280.1	Benzoic acid, 4-methyl-, 2-methylpropyl ester	0.035040	201		
	1282.6	Phenol, 2-methoxy-4-propyl	0.12796	202		
20	1344.6	Eugenol	0.019586	210		
	1351.1	Levodopa	0.034104	211	0.49220	212
	1386.1	Phenol, 4-ethyl-2-methoxy			0.040772	215
	1397.1	1-Naphthalenol	0.063726	216		

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	R.T.*	Name	Whole Oil		NR60D-2H	
			Area%	Peak #	Area%	Peak #
	1403.6	Phenol, 2,4-bis(1,1-dimethylethyl)-	0.054585	217		
	1424.6	Burylated Hydroxytoluene	12.087	218	10.861	219
5	1426.6	Phenol, 4-(2-aminopropyl)-,(ñ)			0.070690	220
	1434.6	Phenol, 4-[2-(methylamino)ethyl]	0.042206	219	.047516	221
	1472.6	Phenol, 2-methoxy-5-(1-propenyl)-,(E)			0.10844	224
	1519.6	3-tert-Butyl-4-hydroxyanisole	0.031443	225	0.031278	227
	1520.1	3-tert-Butyl-4-hydroxyanisole			0.031278	227
10	1536.1	Phenol, 2,6-bis(1,1-dimethylethyl)-4-ethyl-	0.044237	229		
	1538.1	Phenol, 4-ethyl-2-methoxy	0.049476	230		
	1553.6	3-tert-Butyl-4-hydroxyanisole			0.10967	234
	1566.1	Ethanone, 1-(2,3,4-trihydroxyphenyl)			0.070903	238
	1570.6	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	0.055395	237	.092669	240
15	1577.6	Benzaldehyde, 2,4-dihydroxy-3,6-dimethyl	0.027003	238	.0083349	241
	1617.1	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	0.19601	244	.30014	246
	1647.6	Benzeneacetic acid, 3,4-dihydroxy-	0.14553	249		
		Benzeneacetic acid, 4-hydroxy-3-methoxy			0.18419	250
		Phenol, 2,6-dimethoxy-4-(2-propenyl)			.19360	251
20	1686.1	Phenol, 4-methyl-2-nitro	0.13512	252		

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	R.T.*	Name	Whole Oil		NR60D-2H	
			Area%	Peak #	Area%	Peak #
	1706.1	Benzeneacetic acid, 4-hydroxy-3-methoxy-	0.10507	254		
	1718.1	Phenol, 2,6-dimethoxy-4-(2-propenyl)	0.14338	255		
5	1732.6	Benzaldehyde, 4-hydroxy-3,5-dimethoxy	1.2295	256	2.3095	252
	1774.6	Benzoic acid, 2,4-dihydroxy-3,6-dimethyl-, methyl ester			0.027131	256
	1820.6	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	0.39642	262	.32717	260
	1862.1	Benzeneacetic acid, 4-hydroxy-3-methoxy-, methyl ester			0.084137	263
	1872.1	Phenol, 2,4,6-tris(1,1-dimethylethyl)	0.056578	270		
10	1931.1	3,5-di-tert-Butyl-4-hydroxybenzaldehyde	0.14329	277	.15838	269
	1944.1	Benzaldehyde, 3-hydroxy-4-methoxy			0.020640	270
	2006.1	Benzeneacetic acid, 3,4-dihydroxy	0.035096	281		
	2058.1	Phenol, 2,6-dimethoxy-4-(2-propenyl)	0.010906	286		
	2069.1	Benzaldehyde, 4-hydroxy-3,5-dimethoxy			0.060959	289
15	2152.1	Phenol, 2,6-bis(1,1-dimethylethyl)-4-ethyl	0.029731	291		
	2211.6	Phenol, 2,6-bis(1,1-dimethylethyl)-4-ethyl	0.029997	295		
	2172.1	3,5-di-tert-Butyl-4-hydroxybenzaldehyde			0.059165	296

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R.T.*	Name	Whole Oil		NR60D-2H	
		Area%	Peak #	Area%	Peak #
2301.1	Phenol, 2,6-bis(1,1-dimethylethyl)-4-ethyl	0.042017	298	.051196	299
2377.6	Phenol, 2-methyl-4-(1,1,3,3-tetramethylbutyl)			0.045775	302
5 2463.6	Benzaldehyde, 4-hydroxy-3,5-dimethoxy			0.027143	305
2473.1	Phenol, 2,6-bis(1,1-dimethylethyl)-4-ethyl	0.051792	305		
3755.1	Benzaldehyde, 4-hydroxy-(2,4-dinitrophenyl)hydrazone	0.018597	313		

#### 10 V-Additive Lignin

A NR with a high melting point, greater than about 110°C is called V-additive lignin, and may be made using any of the processes described above however, the time during distillation/evaporation process is increased, and the temperature during

15 distillation/evaporation is also increased. Characteristics of V-additive lignin are presented in Table 3d. V-additive lignin is a highly polymerized MNRP, it is commuted to a powder or produced in a flake-like form prior to use. V-additive lignin is a thermoplastic product and is suitable for use within industrial applications, for example as a plasticizer that can be used within foundry resin formulations and admixed with

20 sand, as an asphalt emulsifier, or as a concrete additive to increase the aeration quality of concrete. V-additive lignin may also be used within the automotive industry.

Table 3d: Analysis of V-Additive Lignin

	<u>Properties</u>	<u>V-Additive Lignin</u>
5	Melting Point °C	110-150
	Gasoline Soluble %	1
	Ash %	0.01
	Flash Point	>280
	Density 25C g/cm <sup>3</sup>	1.19
10	Hydroxyl %	1.4
	Methoxyl Content %	5.3
	Colour	Dark Brown
	<b>Chemical Composition</b>	
	Phenolic Fraction	95
15	Hydrocarbon Fraction	0.1
	Rosin-Derived Fraction (acids)	1
	Water	3
	Ester, Aldehyde, Alcohol	0.9

20

**Example 3:** Replacement of phenol within NR-containing PF resins and their use in OSB manufacture

25 The NR produced according to the method of Example 2 is formulated into a resin according to industry standards except that 40% of the phenol content is replaced by the NR. The adhesive resin comprised a formaldehyde:(phenol+NR) ratio of 1.6:1. An adhesive prepared from a Bio-oil-WH (i.e. the whole-oil feedstock), that had not been processed by distillation/evaporation is included for comparison.

30 Typical NR resin formulations involved loading phenol, water and paraformaldehyde into a kettle and heating to 95°C to dissolve the paraformaldehyde. The mixture is cooled to 45°C and the NR added. Caustic (NaOH) is then added to the desired pH thereby solubilizing the NR and initiating the reaction. During the addition of caustic, the mixture is maintained at 45°C for the first caustic addition (approximately 35 2/3 of the amount required). The mixture is then slowly heated to 90°C over a 30 min period over which time the resin is monitored for viscosity and subsequently cooled prior



during which the remaining caustic is added. The resin is maintained at 10°C until use. The resultant formulations are characterized in Table 4.

**Table 4: Adhesive Characterization for OSB**

5

NR portion of resin	Viscosity (cps)	Solids content (%)*	Free CHOH (%)	Gel Time (sec)	pH	Amount of Caustic (wt%)
NR60D-WH	78	41.7	1.21	<600	10.44	7.97
NR60D-2H	81	41.88	1.36	684	10.45	8.6
10 MNRP-1H(70)	120	44.06	1.56	521	10.67	9.57
MNRP-2H(70)	101	43.78	2.11	672	10.46	8.09
Biooil-WH	70	40.37	0.8	733	10.53	7.97

\* determined by heating resin sample at 105°C for 16 hours

15 The OSB's are prepared following standard industrial procedures using one of the adhesive resins listed in Table 4 as well as a control (commercial) resin. The parameters for OSB production are as follows:

Strands: 3 inch poplar from an OSB mill  
 20 Panel type: homogenous  
 Panel thickness: 7/16"  
 Panel size: 18" x 18"  
 Resin content: 2.0% (solids basis)  
 Wax content: 1.5%  
 25 Mat moisture: 5.5%  
 Total Press time: 180 sec  
 Press temperature: 215°C  
 Press pressure: 1350 psi  
 Replication: 4

30

The prepared OSB are tested for the following properties: density, IB (internal bond), MOR (modulus of rupture), and MOE (modulus of elasticity), according to the Canadian product standard for OSB (CSA 0437.1-93, April 1993). Twenty OSB panels

are manufactured using the five resins (4 NR-based resins and one control). The panels are tested right after pressing, without conditioning. The test results are presented in Table 5

**Table 5: Summary of OSB Panel Test Results**

NR-based resin	Density of IB sample	IB (MPa)	MOR (MPa)		MOE (MPa)	Torsion Shear		Thickness Swelling (%)	Water Absorption (%)
			Dry	Wet		Wet	(in.lb)		
Control	670	0.586	34	15.7	4300	40.9		15.4	30
NR60D-WH	670	0.46	37.2	17.6	4600	26.1		18.7	33.6
NR60D-2H	669	0.553	36.3	15.7	4700	36.6		17.7	32.1
MNRP-1H70	671	0.593	35	17.3	4700	34.1		17.9	33.2
MNRP-2H70	670	0.558	29.8	18.1	4000	40		16.3	32.6
Biooil-WH	652	0.419	26	14.9	4100	20.5		18.9	40.1

Panels produced using a resin composition comprising NR, substituted for 40% of phenol, exhibit properties equivalent to that of the commercial PF resin composition. The OSB prepared using NR based resins does not exhibit any difference in appearance compared with OSB's prepared using PF resins. The NR-based resins exhibit better properties than the Biooil-WH (light pitch) based resin that had not been processed using distillation/evaporation. The Biooil-WH bonded panels did not meet OSB and wafer board specifications as set out in CSA Standard 0437.093.

The panels produced using NR-based resins exceeded the CSA Standard (0437.0-93) for all parameters, except for thickness swelling. As the panels are tested right after pressing without conditioning, it is expected that thickness swelling and water absorption could be lowered by conditioning the panels to a constant mass and moisture content prior to the test. Furthermore, as the NR-based resins have a lower viscosity and alkalinity, the adhesive easily penetrates into the veneer and may starve the glue joint. Optimization of the penetrating property of these resins will increase bonding strength and associated properties.

These results indicate that a substantial proportion of phenol within PF resin formulations may be replaced with NR and the resultant adhesive performs as well, or exceeds the performance of commercially available resins. Furthermore, these results indicate that the processing of whole-oil (light pitch) as described herein produces an NR suitable for PF resin use.

**Example 4:** Replacement of phenol within NR-containing PF resins and their use in plywood manufacture

The NR produced according to the method of Example 2 is formulated into a resin according to industry standards except that 40% of the phenol content is replaced by the NR. The adhesive resin comprised a formaldehyde:(phenol+NR) ratio of 1.6:1. NR-based resin formulations were prepared as follows: water (125.4 g; 13.2 wt%) is mixed with soda ash (4.75 g; 0.5 wt%) for 5 min. To this wheat flour (63.7 g; 6.7 wt%) is added and mixed for 10 min. NR (337 g; 35.5 wt%), NaOH (50% solution, 26.6g; 2.8 wt%) and Cocob (55.1 g; 5.8 wt%) are added and mixed for 15 min. A further amount of NR (337.5 g; 35.5 wt%) is added and mixed for 15 min. Commercial plywood resin is also prepared according to industry standards. The resultant formulations are characterized in Table 6.

**Table 6: Adhesive Characterization for Plywood**

NR portion of resin	Viscosity (cps)	Solids content (%) <sup>*</sup>	Free CHOH (%)	Gel Time (sec)	pH	Amount of Caustic (wt%)
NR60D-WH	1385	42.98	0.5	<500	10.44	7.97
NR60D-2H	1120	42.02	0.6	476	10.45	8.6
MNRP-1H(70)	1070	44.35	0.91	446	10.67	9.57
MNRP-2H(70)	1125	44.28	1.48	558	10.46	8.09

<sup>\*</sup> determined by heating resin sample at 105°C for 16 hours

Plywood panels are prepared following standard industrial procedures using one of the adhesive resins listed in Table 5 as well as a control (commercial) resin. The parameters for plywood panel production were as follows:

- Panel construction: 3 ply, 305 x 305 mm (12" x 12"), yellow birch
- Veneer thickness: 1.5 mm
- Veneer moisture: 8.6%
- 10 Glue spread: 20g/ft<sup>2</sup> (215g/m<sup>2</sup>, or 44lb/1000ft<sup>2</sup>)
- Open assembly time: 5 min\*
- Press time: 3,4,5,7 min.
- Press temperature: 160°C
- Replication: 4 per glue
- 15 \*20 min for NR60D-WH

The prepared plywood panels are tested for shear strength under both dry and 48 hour soaked conditions. Twenty OSB panels were manufactured using the five resins (4 NR-based resins and one control). The panels were tested right after pressing, without conditioning. Specimens are tested to failure by tension in the dry condition (average 10 specimens). The test results are presented in Table 7

Table 7: Summary of Plywood Panel Test Results\*

	Glue	Press Time (min)	Shear Strength (MPa)
			Dry Test
5	Commercial Plywood Adhesive	3	3.831 (0.537)
		4	4.030 (0.523)
		5	2.732 (0.425)
		7	3.692 (0.280)
		Avg.	3.571 (0.576)
10	MNRP-1H70	3	3.415 (0.182)
		4	3.586 (0.169)
		5	3.782 (0.354)
		7	3.736 (0.447)
		Avg.	3.629 (0.166)
	MNRP-2H70	3	3.503 (0.201)
		4	3.932 (0.314)
		5	3.129 (0.252)
		7	2.970 (0.334)
		Avg.	3.384 (0.429)
15	NR60D-2H	3	2.697 (0.208)
		4	2.799 (0.192)
		5	3.254 (0.239)
		7	2.624 (0.208)
		Avg.	2.843 (0.283)
	NR60D-WH	3	3.111 (0.270)
		4	3.041 (0.296)
		5	3.347 (0.379)
		7	3.515 (0.305)
		Avg.	3.254 (0.218)
20	NR60D-WH**	3	3.761 (0.490)
		7	2.836 (0.193)
		Avg.	3.298 (0.655)

\* Values in parentheses are standard deviations.

\*\* Open assembly time was 20 min for the panels made with this glue, which was the time interval between applying adhesive on the veneers and closing them together before bonding.

The dry shear strength of the NR-based resins are comparable to the commercial adhesive bonded panel, and all panels meet the minimum shear strength of 2.5 MPa

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required under CSA standard 0112.6-M1977. The NR-based resins have a lower viscosity and alkalinity, and the adhesive may easily penetrate into the veneer and starve the glue joint. Optimization of the penetrating property of these resins will increase bonding strength and associated properties.

5

These results indicate that a substantial proportion of phenol within PF resin formulations may be replaced with an NR fraction obtained from bio-oil for the preparation of adhesives for use in plywood manufacture..

#### 10 **Example 5: Testing of NR60D-2H with PF Adhesives**

##### A) NR60D-2H at 10 and 20%

Eleven 3' x 3' x 0.5" plywood panels are manufactured in order to evaluate the effects of varying concentrations NR60D-2H substitution for phenol in PF resin.

15

#### **Plywood Panel Manufacture**

##### **Blending and Forming**

20

Three different resin compositions are applied to pine veneers (Table 8). This resulted in three groups with a minimum of three panels per group. All applications are made at a 35 lb/1000 ft<sup>2</sup> loading rate. All resins are applied using a plywood glue spreader and applied on a single glue line.

25

Billet lay-up for each panel consists of four plies. The face plies are laid-up parallel to the machine direction and the core plies are laid-up perpendicular to machine direction. Three control panels, four PF/NR60D-2H, at 10% panels (Group NR60-10%), and four PF/NR60D-2H at 20% (Group NR60 - 20%) panels are manufactured in the trial.

Table 8:

	Group ID	No. of Panels	Resin Type	Resin Loading	Pressing Time (sec)
5	Control	3	GP PF Resin (Control)	35 lbs/1000ft <sup>2</sup> single glue line	300
	NR60-10%	4	GP PF/NR 10 Resin	35 lbs/1000ft <sup>2</sup> single glue line	300
	NR60-20%	4	GP PF/NR 20 Resin	35 lbs/1000ft <sup>2</sup> single glue line	300

#### 10      **Pressing and Testing:**

Before pressing, the billets are pre-pressed (cold) at 150 psi for four minutes in a 4' x 8' press. The panels are then transferred for hot pressing to a 3' x 3' press. The panels are pressed under constant pressure control for 300 seconds at 300°F. Pressing is monitored and controlled with a PressMAN© Press Monitoring System. After pressing, 15 the panels are trimmed to 28" x 28" dimensions and hot stacked. Once cooled, the panels are evaluated. The panels are tested for plywood glue bond and flexural creep (CSA standard 0151-M1978).

No resin quality differences are noted visually during panel manufacture. The 20 control and NR substituted resins behaved in the same manner with equal spreadability. The shear data indicates the NR substituted resin performed as well as the control (Table 9). The NR60D-2H (10%) and NR60D-2H (20%) resins both performed comparably to the control, under both test conditions with respect to shear strength. The resins showed exemplary strength characteristics with the ply only failing on the glue bond a maximum 25 of 12% (PG2-88% average wood failure) under both test conditions. The strength of the NR-resin data is further supported by the fact not one sample demonstrated less than 60%, or less than 30%, wood failure under both test conditions.

**Table 9: Test data summary using NR-based plywood shear tests with both NR60D-2H (105) and NR60D-2H (20%) (Average values for ten specimens per panel from 3 panels per group)**

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Test Condition	Property	CSA 0151 Requirement	Units	Control	NR 60 10%	NR60 20%
Vacuum-Pressure Soak:	Shear Strength	No. Req.	psi	89	102	88
	Percent Wood Failure Average	80	%	95	90	88
	Percent Wood Failure ≥ 60	90	%	100	100	100
	Percent Wood Failure ≥ 30	95	%	100	100	100
Boil-Dry Boil:	Shear Strength	No. Req.	psi	79	80	69
	Percent Wood Failure - Average	80	%	91	90	91
	Percent Wood Failure ≥ 60	90	%	93	100	100
	Percent Wood Failure ≥ 30	95	%	100	100	100

**B) NR60D-2H used at 25% for the Preparation of Plywood and OSB Panels**

20

A total of seventeen 3' x 3' x 0.50" OSB, and fifteen 3' x 3' x 0.50" plywood panels were manufactured to evaluate the effects of 25% substitution of NR60D-2H for phenol in PF resin, for both OSB and plywood.

**25 OSB Panel Manufacture**

**Blending and Forming:**



The resins are supplied by Neste in the following formats: Neste PF face control #1, Neste PF core control #2 and Neste PF/NR-60 - 25% (experimental). Three groups of panels are manufactured as indicated in Table 10. The control group (SNC) consists of the Neste face control #1 resin applied to the strands along with commercial E-wax; the strands are then formed into random homogenous mats. The first experimental group (SNE) consists of the substitution of the Neste PF/NR60 - 25% resin for the face control resin in the same manufacturing methodology. The final experimental OSB group (SN) utilizes Neste PF/NR 60-25% on the panel face strands and the Neste core control #2 on the panel core strands. The SN mats are of 50/50 face-core random construction.

TABLE 10: PF AND PF-NR60 RESIN OSB TESTS

Group ID	No. of Panels	Resin Content	PANEL SPECIFICATIONS				
			Construction	Thickness (in.)	Density (lb/ft <sup>3</sup> )	Comments	
15	SNC	8	Neste PF Face resin, 3.5% (Control #1)	Homogenous	0.5	39	OSB control
	SNE*	6	Neste PF/NR 25, 3.5%	Homogenous	0.5	39	OSB Trial
	SN**	3	Face: Neste PF/NR 25, 3.5% Core: Neste PF core resin, 3.5% (Control #2)	50/50 face-core	0.5	39	Face NR Substitute Core Control on OSB

\* NR/RF resin used on the surface and core of the OSB

\*\* NR/PF resin used on surface only

All resins are applied at a 3.5% solids basis. The commercial e-wax is applied at a 1.0% solids basis. All billets are hand formed to yield a density of 39 lb/ft<sup>3</sup> when pressed to a thickness of 0.5".

After formation, the mats are then pressed utilizing a standard OSB pressing cycle. The total pressing time is set to a conservative 400-second cycle to ensure complete cure

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of the applied resin. Pressing is monitored and controlled with a PressMAN© Press Monitoring System.

5 After pressing, the panels are removed, trimmed to 28" x 28" dimensions, and measured for out-of-press thickness and density and the panels are hot-stacked. Upon cooling, the panels are tested (CSA Standard 0437.2 - 93) for: MOR/MOE, IB, bond durability (2hr and 6hr cycles), thickness swell (24hr soak), and linear expansion (ODVPS) as well as flexural creep.

## 10 Plywood Panel Manufacture

### Glue Spreading and Veneer Lay Up

15 Two plywood resins are used for the study. The first resin is Neste PF (plywood control) while the second is Neste PF/NR 25 (plywood experimental). The veneer used for plywood manufacture is pine.

20 The resins are applied to the veneers using a glue spreader. A rate of 35 lbs.per 1000ft<sup>2</sup>, applied on a single glue line is utilized. The lay up consisted of two face veneers, parallel to machine direction, and two core veneers, perpendicular to machine direction, for each panel. Eleven control (Group PNC) and four experimental (Group PNE) panels, are manufactured (Table 11).

TABLE 11: PF AND NR60D-2H at 20% RESIN PLYWOOD SHEAR TESTS

	Group ID	No. of Panels	Resin Content	PANEL SPECIFICATIONS		
				Construction	Thickness (in.)	Comments
	PNC Control	11	35lb/m SGL Neste PF (plywood)	Four ply pine Veneers	0.5	Plywood control
5	PNE (NR-25%)	4	35lb/m SGL Neste PF/NR (plywood)	Four ply pine Veneers	0.5	Plywood test resin

During lay up, gluing time, open assembly time, pre-pressing time and closed  
10 assembly time were measured for each panel.

### Pressing and Testing

After pre-pressing at four minutes and 150 psi, the billets are placed in a press for  
15 final cure and pressing. The first seven control panels (PNC 1-7) are used to establish the  
pressing time. This resulted in the establishment of 300 seconds as the required pressing  
time. Pressing is monitored and controlled via a PressMAN© Press Monitoring System.

After pressing, the panels are then trimmed to 28" x 28" dimensions and hot  
20 stacked. Upon cooling, the panels are evaluated. Testing consisted of glue-bond shear  
and flexural creep evaluation.

Virtually no difference is observed between the control and NR substitution resins.  
Color, viscosity and spreadability for all resins is equal, and all resins behave equally in  
25 a manufacturing situation.

A comparison of the NR substituted resins versus the control (SN, SNE, vs. SNC)  
shows bending and bond properties to be equal between the three groups (Table 12). The  
results indicate, especially with group SN, a drop in bond durability and linear expansion  
30 versus the control. Group SN showed a value of water swell well within the maximum  
requirement (data not included)

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Table 12: SUMMARY OF PF AND PF/NR60 at 25% OSB TESTS

	Property	Req	Units	Control Group (SNC)	NR Surface/ Neste Core (SN)*	NR Surface/NR Core (SNE**)
5	Modulus of Rupture (after pre-conditioning)	Min. 2500	psi	3210	3190	3190
	Modulus of Elasticity (after pre-conditioning)	Min. 450	psi x 1000	479	493	469
10	Internal Bond (after pre-conditioning)	Min. 50.0	psi	56.3	49.7	54.6
	Bond Durability:					
	- MOR after 2HR. BOIL (tested when wet)	Min. 1250	psi	1.8e+07	13101550	14201870
	- MOR after 6 cycle	Min. 1250	psi			
15	*NR/PF resin used on surface only					
	**NR/RF resin used on the surface and core of the OSB					

With respect to the plywood shear testing the results are favourable both against the standard and the control Group (Table 13). A strong bond is indicated by the shear strength performance under both test conditions. Under both conditions 11% or less failure could be attributed to the glue while the maximum allowable is 20% (89% wood failure for Group PNE under boil-dry-boil). A further indicator in the strength of the data is that not one PNE sample showed wood failure values of less than 60% or 30% under both test conditions (100% pass for both requirements on both test regimens).

**Table 13: SUMMARY OF PF AND PF/NR60 at 25% RESIN PLYWOOD SHEAR TESTS**

	Test Condition	Property	CSA 0151 Requirement	Units	Control Group (PNC)	Neste NR/PF (PNE)
5	Vacuum- Pressure Soak:	Shear Strength	No. Req.	psi	82	110
		Percent Wood Failure Average	80	%	87	93
10		Percent Wood Failure $\geq 60$	90	%	93	100
		Percent Wood Failure $\geq 30$	95	%	100	100
	Boil-Dry Boil:	Shear Strength	No. Req.	psi	74	83
		Percent Wood Failure Average	80	%	89	89
15		Percent Wood Failure $\geq 60$	90	%	100	100
		Percent Wood Failure $\geq 30$	95	%	100	100

**Example 6: OSB TESTING OF NR-60 and MNRP**

5 Further tests were carried out at W.K.I. in Germany to assess the industrial performance of NR-containing resins against a commercial PF OSB resin. Control resins, and resins having from 20% to 50% phenol substitution of either NR-60 or MNRP were manufactured and used for testing. Testing of the OSB boards were compared against European Standards for test protocols including V100, EN 300/1997, typically at three press cycles in the range of 12-16 s/mm.

10

Boards were tested according to EN 300/1997 and particularly for Type 4 OSB, for heavy duty load-bearing. Further to the V100 value, the option 2 V100 test (conducted after the boiled samples were dried) was also carried out.

15 **NR-60**

The properties of the NR-60 at 30%, and control resins, and the results of the W.K.I. board tests are given in Table 14.

**Table 14.** Resin specifications, and Properties of the OSB samples using NR-60 at 30% substitution

	Resin #	Control	NR-60
5	% substitution	-	30%
	Molar ratio	2.10	1.87
	NaOH,%	6.0	7.4
	Solids 2h @120°C	42.1	53.5
	Viscosity,cp	370	350
10	Alkalinity test,%	5.92	6.31
	<b>Properties of OSB</b>		
	Density, kg/m	661	681
	IB, N/mm <sup>2</sup>	0.55	0.55
	V100, N/mm <sup>2</sup>	0.24	0.24
15	V100 option 2, N/mm <sup>2</sup>	0.44	0.52
	MOR, N/mm <sup>2</sup>	23.7	23.9
	MOR after boiling	10.8	10.5
	24h swells, %	19.4	18.0
	HCHO, mg	1.19	1.11
20	Moisture, %	4.27	5.29

These results indicate that the NR-60 performed at least as well as the control, while the V100 Option 2 values and swells were improved when compared to the control. The results from the OSB trial were successful and they confirmed results obtained in the lab.

25

Repeated trials using NR-60 based resins at 30% substitution, and OSB made using this resin are present in Table 15.

**Table 15.** Resin specifications, and Properties of the OSB samples using NR-60 at 30% substitution

	Resin #	Control	NR-60
5	% substitution	-	30%
	Molar ratio	2.10	1.84
	NaOH, %	6.0	7.4
	Solids 2h @ 120°C	42.1	43.2
	Viscosity, cp	370	340
10	Alkalinity test, %	5.92	6.36
<b>Properties of OSB: 12s/mm press cycle</b>			
	Density, kg/m	722	726
	IB, N/mm <sup>2</sup>	0.61	0.81
	V100, N/mm <sup>2</sup>	0.19	0.27
15	24h swells, %	16.5	13.7
<b>Properties of OSB: 14s/mm press cycle</b>			
	Density, kg/m	728	722
	IB, N/mm <sup>2</sup>	0.82	0.92
	V100	0.29	0.33
20	24h swells, %	14.1	16.1
	HCHO, mg	2.8	1.7
	Moisture, %	8.1	7.9
<b>Properties of OSB: 16s/mm press cycle</b>			
	Density, kg/m	734	724
25	IB, N/mm <sup>2</sup>	0.93	0.94
	V100	0.34	0.37
	24h swells, %	14.5	14.4



5       These results demonstrate that the properties of the OSB made using NR-60 resins  
exceeded those of the control resin. The use of NR-60 at 30% of phenol indicates that the  
effectiveness of the phenolic resin was equal or even better than the respective ones of the  
control; all wet properties seemed unchanged, while the (free) formaldehyde release was  
substantially reduced. Furthermore, these results demonstrate that the NR-60 product is  
consistent when produced at different times, from different NR60-D batches, and used in  
10   independent trials.

A second series of NR resins were prepared using standard NR-60 products to substitute  
up to 40% of the phenol. These NR-60 substituted resins and the OSB made using these  
resins are compared to a control resin in Table 16.

15

**Table 16.** Resin specifications, and Properties of the OSB samples using NR-60 at 40% substitution

	<b>Resin #</b>	<b>Control</b>	<b>NR-60</b>	<b>Control*</b>	<b>NR-60*</b>
	% substitution	-	40%	-	40
5	Molar ratio	2.10	2.04	2.10	1.80
	NaOH,%	6.10	7.40	6.1	7.4
	Solids 2h @120°C	42.2	44.0	42.0	43.3
	Viscosity,cp	380	340	320	330
	Alkalinity test,%	6.18	6.54	5.50	5.95
10	<b>Properties of OSB: 12s/mm press cycle</b>				
	Density, kg/m	719	716	714	722
	IB, N/mm <sup>2</sup>	0.58	0.50	0.83	0.66
	V100, N/mm <sup>2</sup>	0.20	0.12	0.36	0.35
	24h swells, %	17.6	19.0	14.7	15.5
15	<b>Properties of OSB: 14s/mm press cycle</b>				
	Density, kg/m	736	726	725	730
	IB, N/mm <sup>2</sup>	0.71	0.73	0.92	0.93
	V100, N/mm <sup>2</sup>	0.30	0.24	0.39	0.35
	24h swells, %	17.4	17.6	14.7	14.2
20	MOR before	25.2	23.5	24.6	21.2
	- after boiling	7.4	5.9	6.7	5.6
	HCHO, mg	2.4	1.3	3.2	0.8
	Moisture, %	8.4	8.4	8.3	8.3
	<b>Properties of OSB: 16s/mm press cycle</b>				
25	Density, kg/m	742	727	726	726
	IB, N/mm <sup>2</sup>	0.65	0.65	1.01	0.94
	V100	0.34	0.20	0.43	0.32
	24h swells, %	17.4	19.6	15.7	15.3

\*separate trail using different NR-60

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Collectively the results in Table 16 demonstrate that, both dry and wet, the properties of the NR-60 OSB at 40% phenol substitution exceeded those of the OSB boards produced with the commercial PF resin (control). The free formaldehyde of NR-60 boards was lower than that of the control. In general, the OSB board properties of the NR-60 based resin met or exceeded the control resin board properties, and the board properties of the NR-60 resin met or exceeded most of the control resin OSB board properties. Furthermore, batch -to-batch consistency of NR-60 is observed since both NR-60 based resins performed equally as well.

#### 10 MNRP

Resins comprising 20, 40 and 50% MNRP substitution, in place of phenol were also evaluated, and the results are presented in Tables 17, 18 and 19, respectively.

**Table 17.** Resin specifications, and Properties of the OSB samples using MNRP at 20% substitution

	<b>Resin #</b>	<b>Control</b>	<b>MNRP</b>
5	% substitution	-	20%
	Molar ratio	2.10	2.14
	NaOH,%	6.10	6.55
	Solids 2h @120°C	42.1	41.5
	Viscosity,cp	360	370
10	Alkalinity test. %	5.67	5.53
	<b>Properties of OSB: 12s/mm press cycle</b>		
	Density, kg/m	726	737
	IB, N/mm <sup>2</sup>	0.68	1.03
	V100, N/mm <sup>2</sup>	0.26	0.37
15	24h swells, %	14.9	13.3
	<b>Properties of OSB: 14s/mm press cycle</b>		
	Density, kg/m	726	733
	IB, N/mm <sup>2</sup>	0.61	0.75
	V100, N/mm <sup>2</sup>	0.25	0.27
20	24h swells, %	16.6	13.9
	MOR, N/mm <sup>2</sup>	23.9	25.3
	MOR retention, %	27.6	23.4
	HCHO, mg/100gm	2.5	1.4
	Moisture, %	8.0	8.0
25	<b>Properties of OSB: 16s/mm press cycle</b>		
	Density, kg/m	734	737
	IB, N/mm <sup>2</sup>	0.95	0.79
	V100, N/mm <sup>2</sup>	0.35	0.25
	24h swells, %	15.5	14.4

**Table 18.** Resin specifications, and Properties of the OSB samples using MNRP at 40% substitution

	Resin #	Control	MNRP	MNRP
5	% substitution	-	40%	40%
	Molar ratio	2.10	2.10	2.10
	NaOH,%	6.10	7.65	7.6
	Solids 2h @120°C	42.0	44.3	43.4
	Viscosity,cp	320	340	320
10	Alkalinity test,%	5.50	6.44	6.28
<b>Properties of OSB: 12s/mm press cycle</b>				
	Density, kg/m	714	733	725
	IB, N/mm <sup>2</sup>	0.83	0.78	0.77
	V100, N/mm <sup>2</sup>	0.36	0.32	0.27
15	24h swells, %	14.7	16.8	17.4
<b>Properties of OSB: 14s/mm press cycle</b>				
	Density, kg/m	725	742	730
	IB, N/mm <sup>2</sup>	0.92	1.01	0.91
	V100, N/mm <sup>2</sup>	0.39	0.28	0.35
20	24h swells, %	14.7	16.5	14.4
	MOR, before	24.6	23.7	24.0
	MOR,after boiling	6.76	5.8	5.6
	HCHO, mg	3.2	1.8	2.0
	Moisture, %	8.3	8.1	7.8
25	<b>Properties of OSB: 16s/mm press cycle</b>			
	Density, kg/m	726	728	730
	IB, N/mm <sup>2</sup>	1.01	0.98	0.96
	V100, N/mm <sup>2</sup>	0.43	0.34	0.37
	24h swells, %	15.7	17.0	16.5

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**Table 19.** Resin specifications, and Properties of the OSB samples using MNRP at 50% substitution

	Resin #	Control	MNRP
	% substitution	-	50%
5	Molar ratio	2.10	2.10
	NaOH, %	6.10	7.55
	Solids 2h @120°C	42.0	43.5
	Viscosity, cp	475	350
	Alkalinity test, %	5.50	5.55
10	<b>Properties of OSB: 12s/mm press cycle</b>		
	Density, kg/m	724	718
	IB, N/mm <sup>2</sup>	0.99	0.61
	V100, N/mm <sup>2</sup>	0.36	0.18
	24h swells, %	14.8	17.6
15	<b>Properties of OSB: 14s/mm press cycle</b>		
	Density, kg/m	729	726
	IB, N/mm <sup>2</sup>	0.98	0.76
	24h swells, %	15.0	16.3
	MOR, before boiling	22.8	24.2
20	MOR, after boiling	7.2	4.6
	HCHO, mg	3.3	1.6
	Moisture, %	8.1	8.6
	<b>Properties of OSB: 16s/mm press cycle</b>		
	Density, kg/m	747	728
25	IB, N/mm <sup>2</sup>	1.03	0.84
	V100, N/mm <sup>2</sup>	0.43	0.28
	24h swells, %	16.3	16.5

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These results indicate that the MNRP-based resin is as or more reactive than the control resin, since the best results were obtained at shortest press cycle. It is also notable that the swelling values are low. At 40% substitution MNRP produced OSB boards that were comparable to control OSB boards even at short press cycles. At 50% substitution with MNRP, the board properties were reduced as compared to the control's, and longer press cycles were required to achieve satisfactory results.

#### Example 7: Analysis of MNRP based resin

A set of panels 28" X 28" were prepared using strands from Ainsworth or Drayton Valley AB. A core and surface resin were used for the preparation of the pannels. The core resin was MDI (Rubinate 1840), and the surface resin was either a control (commercial) or MNRP resin at the concentrations listed in Table 20.

Table 20: Resins used for panel preparation.

Panel Set			PF Resin			
			Urea %	Solids %	Viscosity cp @ 25°C	Alkalinity %
20	2	ACM control	7.0	49.9	160	3.18
	3	MNRP 30%	4.8	45.0	250	6.50
	4	MNRP 30%	6.8	52.5	160	3.50
	5	Ainsworth control	-	-	-	-
	7	MNRP 50%	7.0	53.2	150	3.63
25	8	MNRP 30%	12.0	51.4	175	3.46

The panels were prepared having a wax content of 1.0%, using random orientation of strands (face/core 55/45), with a target thickness of 7/16", press temperature of 400°F, and press closing 30 sec. Panels were tested for Modulus of Rupture, Modulus of elasticity, Internal Bond (all CSA 0437), Thickness swell, Water Absorption and Edge Swell. The results are presented in Table 21.

Table 21: Analysis of OSB prepared using resins and panel sets defined in Table 20

Panel Set	2	3-1*	3-2*	4*	5	7*	8*
Density, kg/m <sup>3</sup>	609	622	618	634	615	640	603
5 Hot IB, N/mm <sup>2</sup>	0.352	0.407	0.388	0.381	0.392	0.272	0.359
IB dry, N/mm <sup>2</sup>	0.267	0.300	0.329	0.386	0.268	0.341	0.207
IB wet, N/mm <sup>2</sup>	0.022	0.042	0.024	0.033	0.024	0.015	0.028
MOR dry, N/mm <sup>2</sup>	16.94	35.71	19.05	26.05	19.32	11.31	27.71
MOR wet, N/mm <sup>2</sup>	5.67	6.45	6.08	5.57	4.28	2.74	5.51
10 MOE dry N/mm <sup>2</sup>	2728.2	3566.4	2606.1	3297.3	3553.5	2246.1	4223.7
MOE wet N/mm <sup>2</sup>	660.4	679.4	647.0	546.5	491.5	302.1	542.6
Swells, %, **	28.13	25.08	26.56	30.94	26.09	30.62	19.29
% after wet test	44.7	40.2	47.5	43.5	47.2	46.5	45.6

\* MNRP resin

15 \*\*at 24h at 20°C

These results indicate that MNRP substituted resins, at either 30 or 50% produce OSBs that perform as well or better than those of the control resin formulations.

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All citations are herein incorporated by reference.

The present invention has been described with regard to preferred embodiments. However, it will be obvious to persons skilled in the art that a number of variations and modifications can be made without departing from the scope of the invention as described herein.

25



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**THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OF PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:**

1. A natural resin (NR) characterized by comprising:
  - i) a free phenol content from about 0.001% to about 0.1% (w/w);
  - ii) a total phenolic content from about 35% to about 80% (w/w); and
  - iii) a pleasant smoky odour.
2. The NR of claim 1 further characterized by comprising
  - i) a pH from about 2.0 to about 3.0;
3. The NR of claim 1, wherein the NR is a liquid NR, characterized by comprising:
  - i) a water content of from about 2 to about 20 wt%;
  - ii) an acids content of from about 0.1 to about 5.0 wt%;
  - iii) an average molecular weight (wet)/(dry) of from about (250-350)/(280-380) Daltons,
  - v) a viscosity at 70°C from about 10 to about 130 (cSt); and
  - vi) a pH from about 2.0 to about 5.0.
4. The NR of claim 3 further characterized by comprising:
  - i) a net caloric value of about 4355 cal/g (18.22 MJ/kg); and
  - ii) a gross caloric value of about 4690 cal/g (19.62 MJ/kg).
5. The NR of claim 1, wherein the NR is a solid NR, characterized by comprising:
  - i) a water content of from about 1 to about 6 wt%;
  - ii) an acids content of from about 0.1 to about 5.0 wt%;
  - iii) an average molecular weight (wet)/(dry) of from about (300-450)/(350-500) Daltons;
  - iv) a pH from about 2.0 to about 5.0; and
  - v) which is solid at room temperature.

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6. The NR of claim 5 further characterized by comprising:
  - i) a net caloric value of about 4355 cal/g (18.22 MJ/kg); and
  - ii) a gross caloric value of about 4690 cal/g (19.62 MJ/kg).
7. A resin composition comprising the NR of claim 1.
8. The resin composition of claim 7 wherein said resin is an adhesive resin, and said NR is present within said resin composition from about 1% to about 40% (w/w).
9. A resin composition comprising the liquid NR of claim 3.
10. A resin composition comprising the liquid NR of claim 5.
11. The resin composition of claim 7, comprising a phenol formaldehyde resin, wherein a portion of the formaldehyde of said phenol-containing formaldehyde resin is replaced with NR.
12. The adhesive composition of claim 11 wherein NR replaces up to about 50% of said formaldehyde content within said phenol-containing formaldehyde resin.
13. The adhesive composition of claim 12 comprising a formaldehyde:phenol ratio from about 1.2:1 to about 3:1.
14. The adhesive composition of claim 13 wherein the formaldehyde:phenol ratio is 1.6:1.
15. The resin composition of claim 7, comprising a phenol formaldehyde resin, wherein up to about 100% of the phenol content, of said phenol-containing formaldehyde resin is replaced with NR.
16. A product prepared using the resin composition of claim 7.

17. A product prepared using the resin composition of claim 9.
18. A product prepared using the resin composition of claim 10.
19. The product of claim 16 comprising, an industrial resin product.
20. The product of claim 19, wherein said industrial resin product is selected from the group consisting of laminated wood, plywood, particle board, high density particle board, oriented strand board, medium density fiber board, hardboard or wafer board, mouldings, linings, insulation, foundry resins, asphalt, concrete, brake linings, and grit binders.
21. A method of preparing a natural resin (NR) comprising:
  - i) liquefying wood, wood bark or other biomass using fast pyrolysis in order to produce vapours and char;
  - ii) removing said char from said vapours;
  - iii) recovering said vapours to obtain a liquid product; and
  - iv) processing said liquid product using distillation/evaporation to produce said NR.
22. The method of claim 21 wherein, said step of recovering comprises obtaining said liquid product from a primary recovery unit, a secondary recovery unit, or both a primary and a secondary recovery unit.
23. The method of claim 22 wherein said step of processing comprises pretreating said liquid product prior to said distillation/evaporation.
24. The method of claim 23 wherein said pretreating comprises adding water to said liquid product prior to said distillation/evaporation.
25. The method of claim 21 wherein said step of processing further comprises adding water to said NR obtained following distillation/evaporation.

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26. A natural resin prepared according to the method of claim 21.
27. A resin composition comprising the natural resin of claim 26.
28. The resin composition of claim 27 wherein said resin composition is an adhesive composition.
29. An industrial product prepared using the adhesive composition of claim 28.
30. The product of claim 29, wherein said industrial resin product is selected from the group consisting of laminated wood, plywood, particle board, high density particle board, oriented strand board, medium density fiber board, hardboard or wafer board, mouldings, linings, insulation, foundry resins, asphalt, concrete, brake linings, and grit binders.



# INTERNATIONAL SEARCH REPORT

Intern: 31 Application No

PCT/CA 00/00868

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L61/06 C08H5/04 C09J161/06 C08G16/02 C08L61/24  
C09J161/24 C10C5/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L C08H C09J C08G C10C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E, L	CA 2 228 418 A (ENSYN TECHNOLOGIES INC., CA) 30 July 1999 (1999-07-30) the whole document	1-30
A	US 4 942 269 A (CHUM HELENA L ET AL) 17 July 1990 (1990-07-17) cited in the application column 3, line 57 -column 8, line 68; claims; examples	1-30
A	US 4 209 647 A (GALLIVAN ROBERT M ET AL) 24 June 1980 (1980-06-24) cited in the application the whole document	20-27



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

23 October 2000

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/CA 00/00868

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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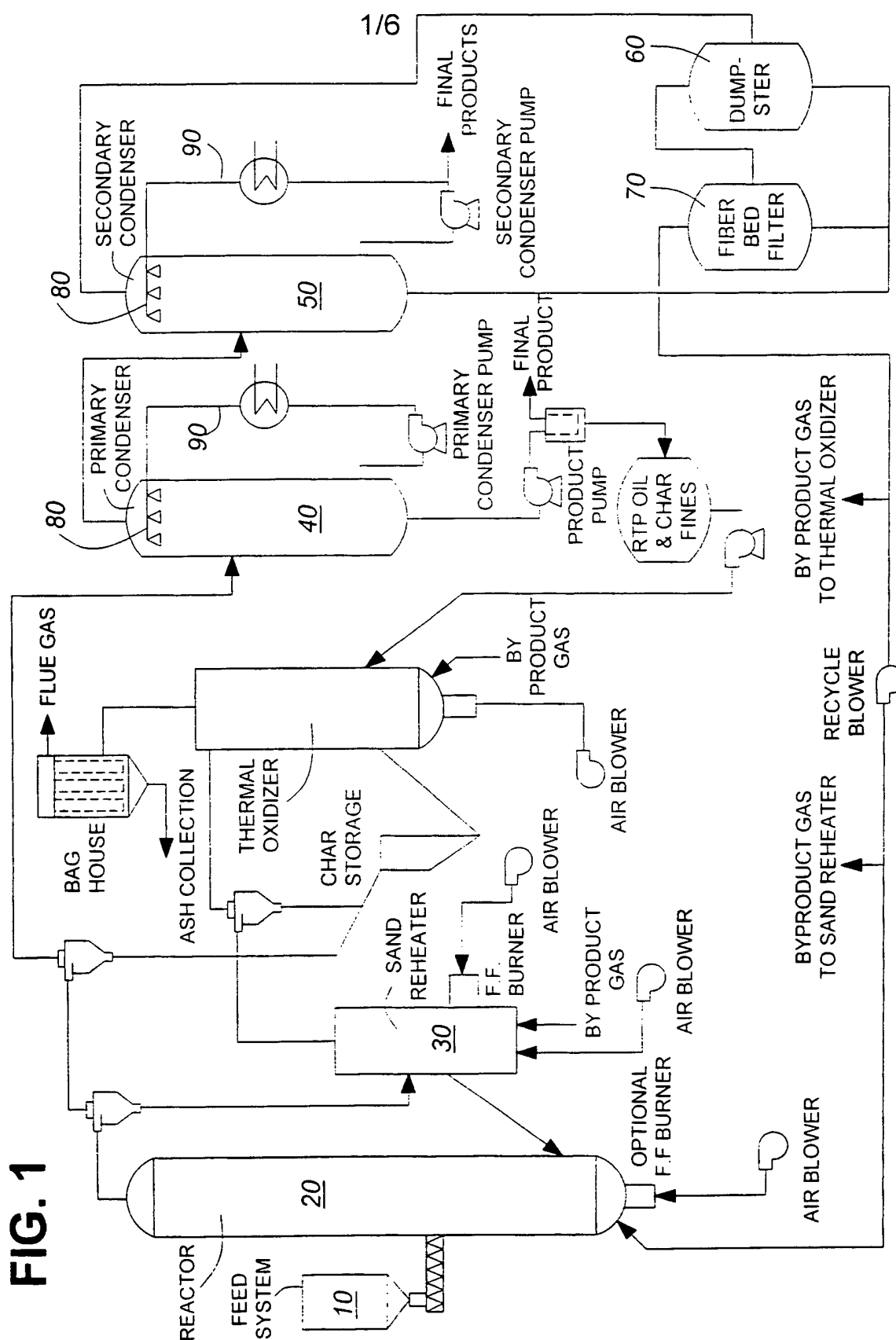
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International Application No

PCT/CA 00/00868

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**FIG. 1**



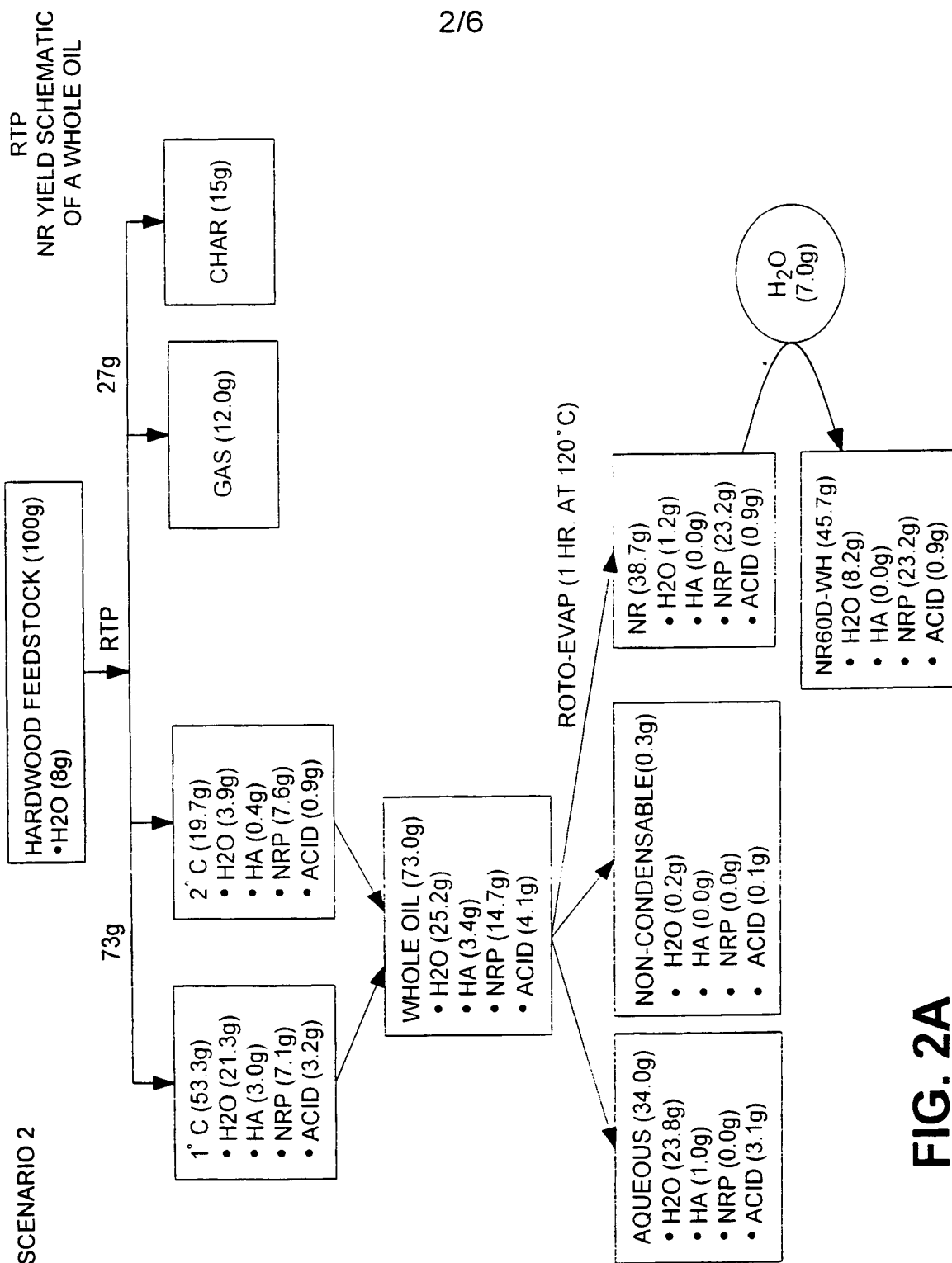


FIG. 2A



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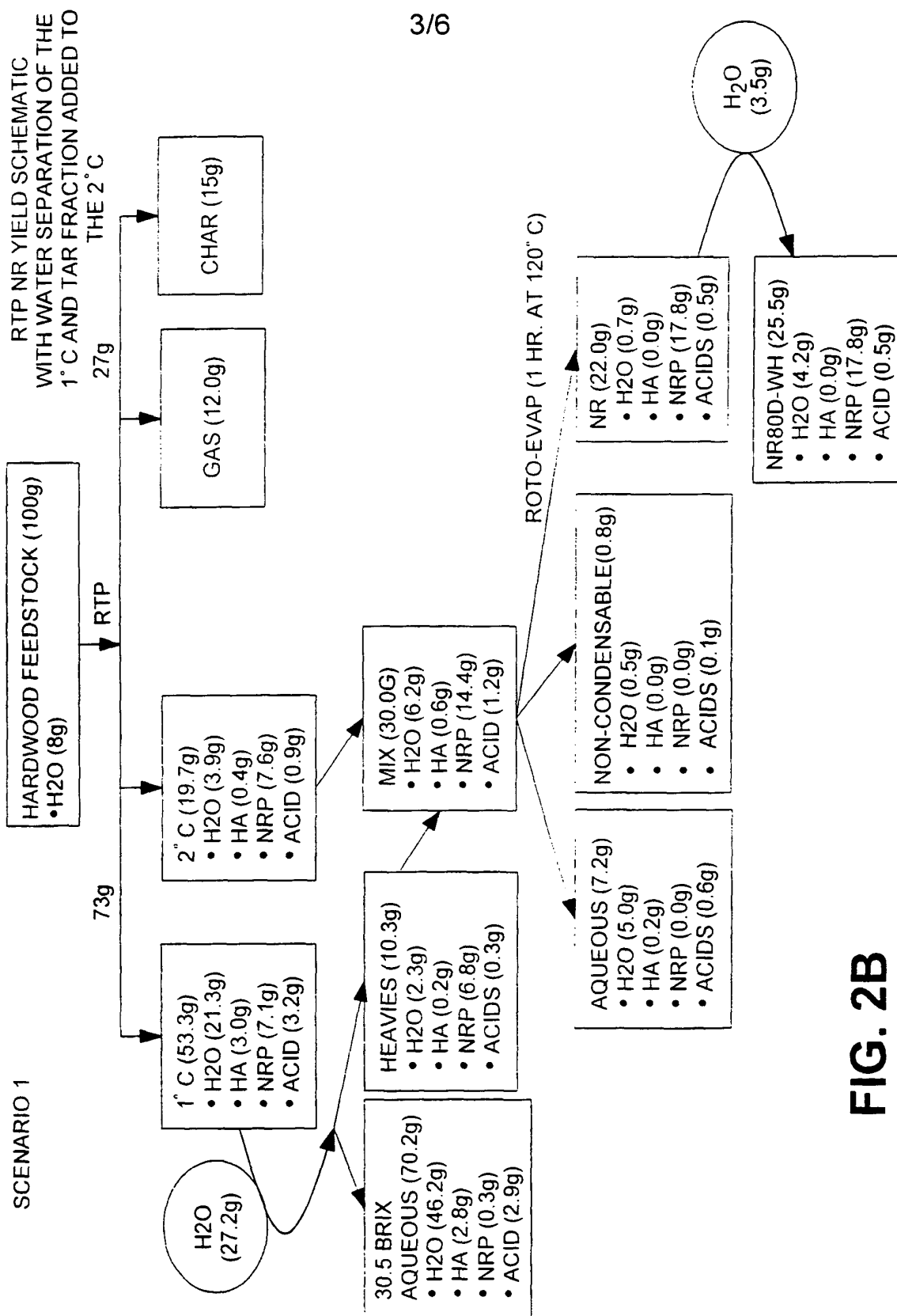


FIG. 2B





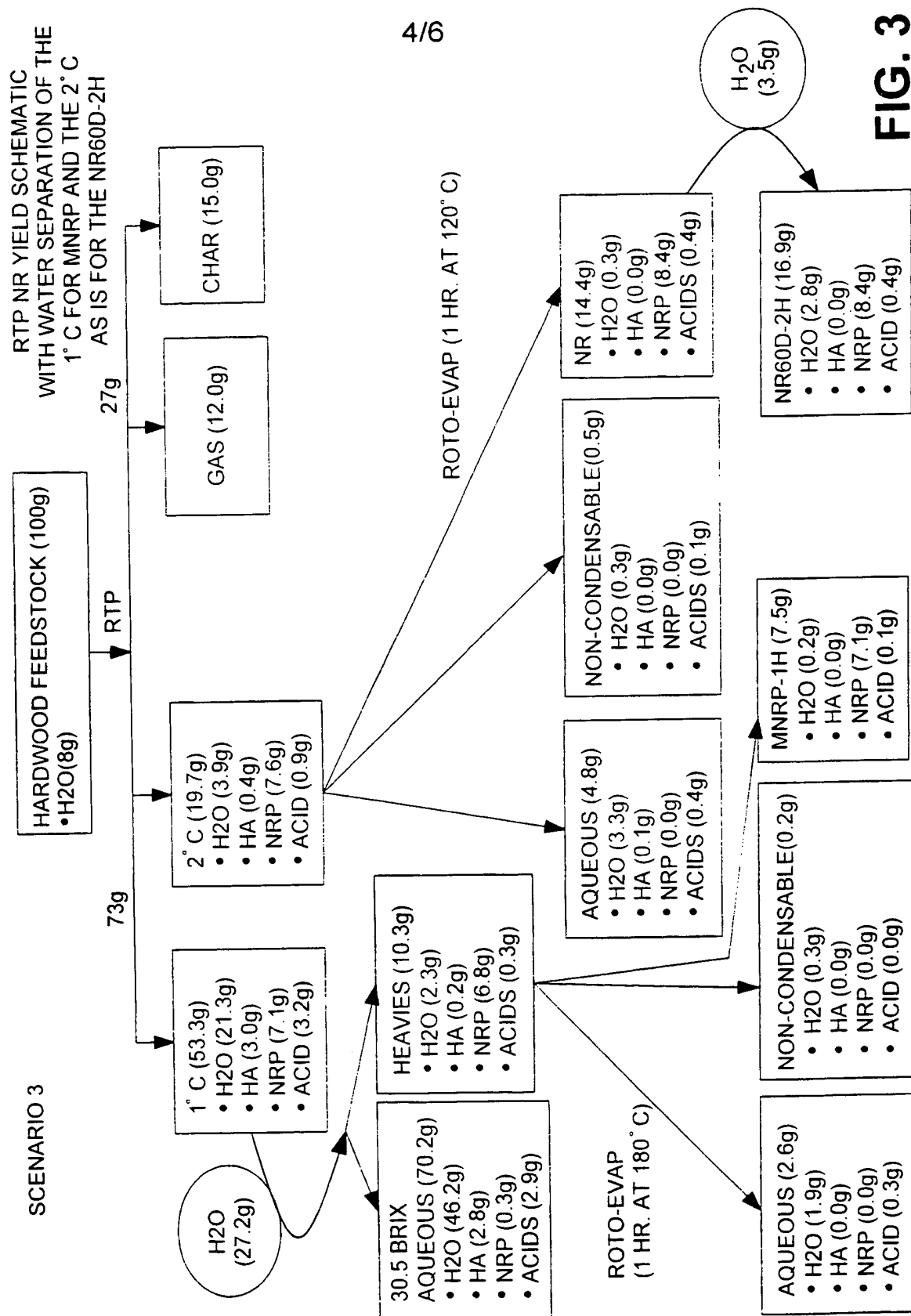
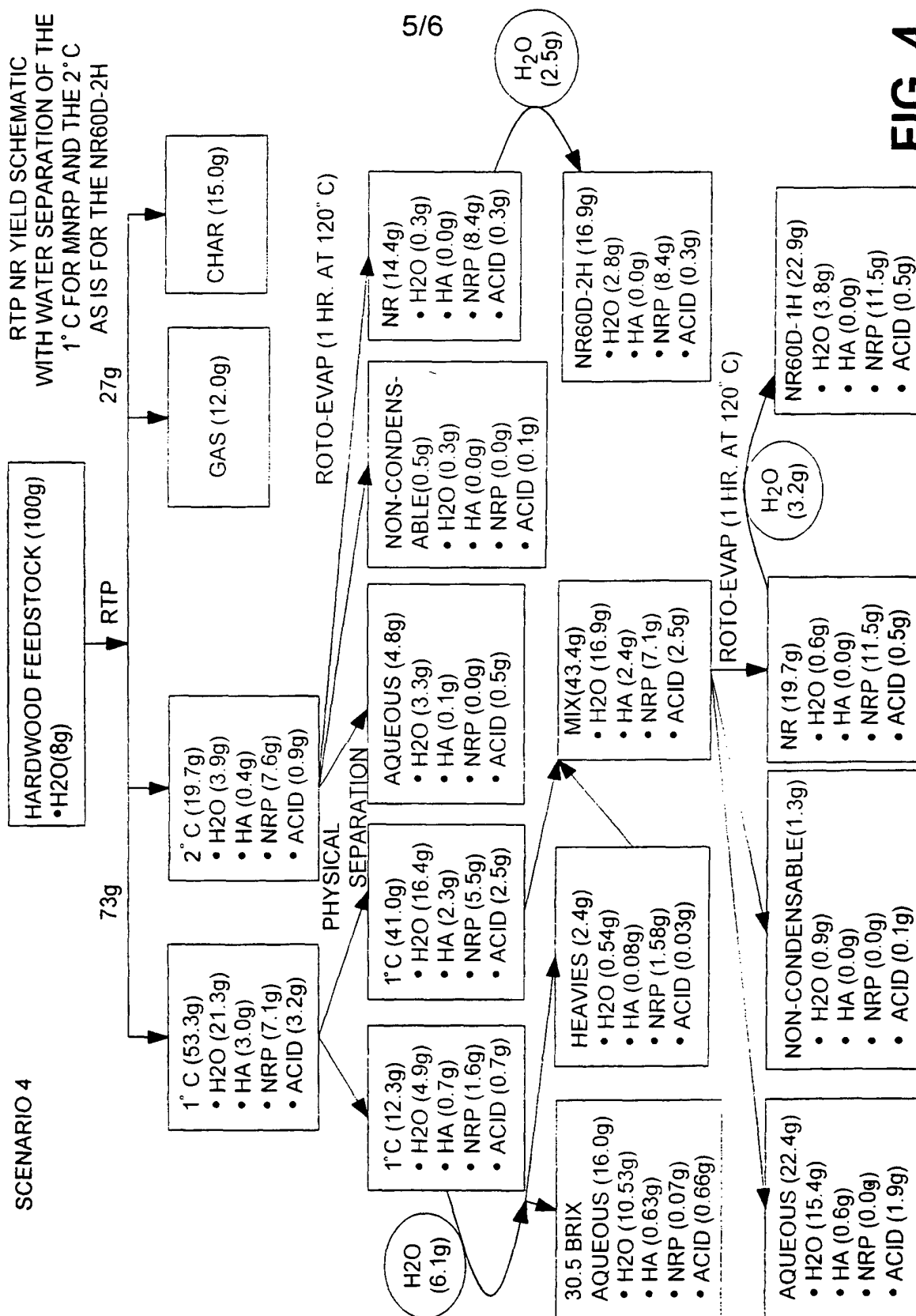


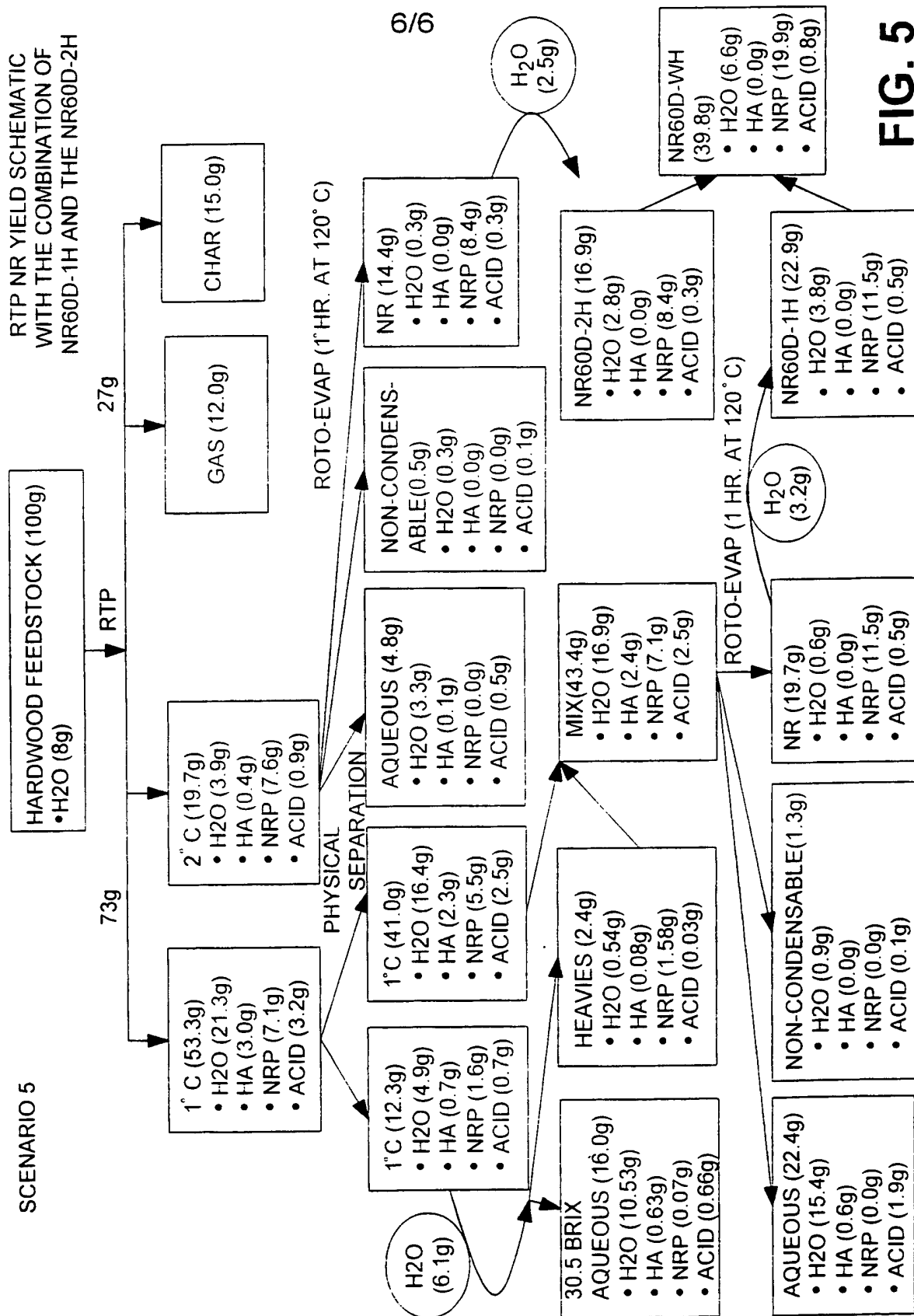
FIG. 3





**FIG. 4**



**FIG. 5**



# INTERNATIONAL SEARCH REPORT

Intern: 31 Application No  
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<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 7 C08L61/06 C08H5/04 C09J161/06 C08G16/02 C08L61/24 C09J161/24 C10C5/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08L C08H C09J C08G C10C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
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A	US 4 209 647 A (GALLIVAN ROBERT M ET AL) 24 June 1980 (1980-06-24) cited in the application the whole document	20-27
	-/--	
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 23 October 2000		Date of mailing of the international search report 30/10/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Hutton, D





# INTERNATIONAL SEARCH REPORT

Intern: al Application No  
PCT/CA 00/00868

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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## INTERNATIONAL SEARCH REPORT

Internat'l Application No

PCT/CA 00/00868

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NOTIFICATION CONCERNING  
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(PCT Administrative Instructions, Section 411)

To:

SECHLEY, Konrad, A.  
Gowling Lafleur Henderson LLP  
Suite 2600  
160 Elgin Street  
Ottawa, Ontario K1P 1C3  
CANADA

BY: ENSYN

Date of mailing (day/month/year)  
24 October 2000 (24.10.00)Applicant's or agent's file reference  
O8-878545WO1

## IMPORTANT NOTIFICATION

International application No.  
PCT/CA00/00868International filing date (day/month/year)  
28 July 2000 (28.07.00)International publication date (day/month/year)  
Not yet publishedPriority date (day/month/year)  
29 July 1999 (29.07.99)

Applicant

ENSYN GROUP, INC. et al

1. The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
2. This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.
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<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
29 July 1999 (29.07.99)	09/364,610	US	26 Sept 2000 (26.09.00)

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## PATENT COOPERATION TREATY

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NOTIFICATION OF RECEIPT  
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12.03.01

Applicant's or agent's file reference

08-878545W01

## IMPORTANT NOTIFICATION

International application No.

PCT/CA 00/00868

International filing date (day/month/year)

28/07/2000

Priority date (day/month/year)

29/07/1999

Applicant

ENSYN GROUP, INC. et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority considers the following date as the date of receipt of the demand for international preliminary examination of the international application:

22/02/2001

2. This date of receipt is:

- ☒ the actual date of receipt of the demand by this Authority (Rule 61.1(b)).  
☐ the actual date of receipt of the demand on behalf of this Authority (Rule 59.3(e)).  
☐ the date on which this Authority has, in response to the invitation to correct defects in the demand (Form PCT/IPEA/404), received the required corrections.

3. ☐ **ATTENTION:** That date of receipt is **AFTER** the expiration of 19 months from the priority date. Consequently, the election(s) made in the demand does (do) not have the effect of postponing the entry into the national phase until 30 months from the priority date (or later in some Offices) (Article 39(1)). Therefore, the acts for entry into the national phase must be performed within 20 months from the priority date (or later in some Offices) (Article 22). For details, see the *PCT Applicant's Guide*, Volume II.

- ☐ (If applicable) This notification confirms the information given by telephone, facsimile transmission or in person on:

4. Only where paragraph 3 applies, a copy of this notification has been sent to the International Bureau.

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